

A TEXT-BOOK OF INORGANIC CHEMISTRY

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EXTRACTS FROM THE PREFACE TO THE FIRST EDITION

THE present text-book is primarily intended for students who have completed an introductory course of Matriculation standard, although the more elementary parts of the subject are included so as to make the book complete in itself. It is not written for any particular examination, but should meet the requirements in Inorganic Chemistry of students preparing for the examinations of the Intermediate and Pass B.Sc. of British universities. Brief accounts of technical processes and the elements of Physical Chemistry are included, with worked examples on the latter.

The Atomic Theory and the Periodic Law have been given prominence, since their neglect unfailingly leads to obscurity and triviality.

Limitations of space prevented more than a bare mention of most of the so-called "Rare Elements", many of which are now of great importance in chemical industry and form part of articles familiar in everyday life. Their chemical properties are also in many cases of unusual interest.

A short account of Werner's theory is given, since the classical theory of Valency, which is of fundamental importance in the somewhat monotonous uniformity of the chemistry of carbon, proves inadequate when any but the very simplest compounds of the remaining elements are under consideration.

The physical properties of substances (densities, boiling points, etc.) have been compiled from the most recent sources, in the hope that the book may also prove useful for reference purposes.

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A TEXT-BOOK OF INORGANIC CHEMISTRY

CHAPTER I

PURE SUBSTANCES AND MIXTURES

Different kinds of bodies.—Different materials may be distinguished from one another by their properties, the most obvious being the *physical state*: *solid*, *liquid* or *gaseous*. Many bodies having the same physical state may be distinguished. These differences we express by saying that the bodies differ in *composition*. In beginning the study of Chemistry we meet with a large number of new substances. Solids may differ in *colour*, e.g. blue copper sulphate, green ferrous sulphate, red potassium dichromate, dark purple chrome alum. Differences in *density* are shown, e.g. by lead nitrate and alum, the first being much heavier for an equal volume than the second. Solids may differ in *crystalline form*; alum crystallises in octahedra, rock salt in cubes.

Solids in which the crystalline form is absent are said to be *amorphous*. Fragments obtained on breaking crystals have sharp edges and plane faces, or show a *crystalline fracture*, whereas the fractured pieces of an amorphous solid such as glass or pitch show curved faces like the inside of a shell, and hence are said to show a *conchoidal fracture* (Fig. 1).

A further method of distinguishing solids is by their *solubility* in liquids. When finely-powdered lead nitrate and barium sulphate, both heavy white powders, are separately stirred with hot water, the first dissolves, whilst the second remains undissolved.

Solids when heated usually melt at characteristic temperatures called their *melting points*. Nitre melts at 336° ,* potassium chlorate at 357° , "hypo" at 48° , rock salt at 801° , barium sulphate at 1580° .

Liquids may differ in colour, density, and *boiling point*. Some have characteristic odours. The *freezing point* of a pure liquid is usually the same as the melting point of the solid obtained from it by cooling. Some

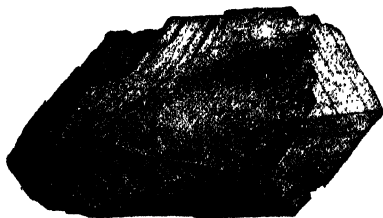


FIG. 1.—Calcite.

Showing conchoidal and crystalline fracture in the same material. (After Miers).

* Temperatures throughout are in degrees Centigrade.

liquids flow less readily than others (*e.g.* treacle and water), or have greater *viscosity*.

The existence of different kinds of gases was not clearly recognised until about 1765-75, when Cavendish and Priestley distinguished several gases differing from atmospheric air. The differences become clear on comparing jars containing the following gases : oxygen, hydrogen, carbon dioxide, nitric oxide, and chlorine.

By simple *observation* chlorine is seen to have a greenish-yellow colour, whilst the other gases are colourless. These colourless gases may be distinguished by appropriate *experiments*.

Remove the glass plates from the jars so as to bring the gases in contact with the air. Nothing occurs except with the nitric oxide, which produces deep red fumes.

Pour a little lime water into the other jars and shake. The lime water is unchanged in appearance in all the jars except that containing carbon dioxide, in which it becomes turbid and white.

Insert a lighted taper into each of a new set of jars of the gases. In oxygen it burns with a brilliant flame, in chlorine with a smoky red flame, but in the other jars it is extinguished. The hydrogen itself, however, takes fire and burns with a pale flame.

A jar of carbon dioxide is held over a large beaker counterpoised on a balance, and slowly inverted so as to pour the gas into the beaker : the latter sinks, showing that carbon dioxide is heavier than air, and has passed into the beaker. A taper inserted into the beaker is extinguished.

A jar of hydrogen is opened, mouth downwards, and slowly inclined so as to pour the gas upwards into an inverted counterpoised beaker. The beaker rises, showing that hydrogen is lighter than air.

Gases, therefore, differ in density, colour, combustibility, capacity for supporting combustion, and action on lime water.

Pure substances.—Crystals of copper sulphate differ in size, often in shape, yet all are composed of the same *pure substance* ; in so far as composition is concerned no account is taken of accidental circumstances such as size or shape. The two kinds of phosphorus, white and red, differ entirely in appearance and properties. Although they consist of the same *material*, phosphorus, they are two different *substances*, each having specific properties by means of which it may be recognised.

The possibility of arranging materials in groups of substances reduces the complexity and scope of their study, because a large number of individual *bodies* may belong to one group, *i.e.* be composed of the same *substance*. The fact that bodies may be arranged in such groups is the fundamental law of chemistry. **Descriptive Chemistry** may be defined as the science dealing with the preparation and properties of substances, and the relations which exist between them.

In some cases there is difficulty in defining the properties of bodies, with the view of placing them in groups of substances. A piece of granite has different properties in different parts ; and if we base our definition on identity of properties, we shall apparently require an in-

finite number of groups to accommodate all the possible liquids produced by adding salt to water in varying proportions. These difficulties are removed by closer study.

Homogeneous and heterogeneous bodies.—Bodies differ according to the properties of their component parts. A body such that all the parts into which it can be divided by mechanical means have identical properties is called a **homogeneous** (or *uniform*) **body**. Glass, water, and air are homogeneous bodies. All pure substances, in the strict sense, are homogeneous bodies, but the converse, as we shall see, is not true.

A body having different properties in different parts is called a **heterogeneous** (or *non-uniform*) **body**. A piece of **granite** is an aggregate of three different minerals. One is pink or grey, opaque, and capable (though with difficulty) of being scratched with a knife; it is felspar. A second is colourless, transparent, and too hard to scratch with a knife; this is quartz. The third forms thin grey, or black, plates, which can be split by a knife into very thin leaves; it is mica.

Since the parts of aggregates such as **granite** are separable by mechanical means, heterogeneous bodies are often called *mechanical mixtures*. The separate parts of a heterogeneous body are called **phases**. Quartz, felspar, and mica are three phases in granite. A mixture of ice and water consists of two phases, whilst a homogeneous body, even if divided into several parts in space, is only a single phase.

The parts of a heterogeneous body are not always so sharply separated as those in granite. Quartz crystals often show brown colouring in different parts ("smoky quartz"); the depth of the colour, due to impurities, may shade off from one part of the crystal to another and it is difficult to fix any place where definite colour change occurs.

The ultramicroscope.—The definitions of homogeneous and heterogeneous bodies are only relative. Milk may seem homogeneous to the eye but is seen under the microscope to contain globules of butter-fat floating in a liquid. In some cases heterogeneity, not shown even by the microscope, may be revealed by the scattering of light.

Although the atmosphere may appear quite clear in ordinary daylight, yet if a beam of strong sunlight passes through it the path of the beam can be seen if there is dust or smoke in the air, because of the light scattered by the dust particles (see p. 8). Very fine particles suspended in a liquid may be detected in a similar way. This is shown by the following experiment.

A few drops of a solution of gum mastic in alcohol are added to water in a glass trough and stirred: the liquid appears clear, but when a beam of light from a lantern is passed through the water, before and after adding the mastic, it will be found that little light can be seen passing through the clear water, but that water to which mastic has been added shows the path of the light as a bright, cloudy beam, called a **Tyndall cone**. The same effect

appears in a ray of sunlight passing through dusty air; particles of dust may be seen floating about in the beam.

An instrument making use of this principle, the **ultramicroscope**, consists (Fig. 3) of a microscope with the object-glass dipping into the liquid to be examined, contained in a small glass cell. A powerful beam of light is brought to a focus in the liquid by a lens. The suspended particles are revealed by the light scattered from them, and they appear as bright specks.

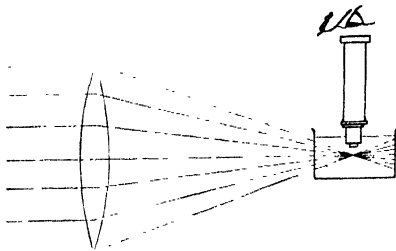


FIG. 3.—Diagram of ultramicroscope.

(1 *micron* = $1\mu = 0.001$ mm.); the ultramicroscope reveals particles down to 5×10^{-7} cm., or $5m\mu$ (1 *millimicron* = $1m\mu = 10^{-6}$ mm.), or about one-hundredth the wavelength of visible light. With the electron microscope, resolution below 50Å. is possible (Å. = Ångström unit = 10^{-8} cm.).

By the action of phosphorus on gold chloride solution, ruby-red clear solutions are obtained, which, as the ultramicroscope shows, contain particles about $5m\mu$ in diameter. Suspensions containing ultramicroscopic particles which do not settle out on standing and pass through filter paper, are called **colloidal solutions**. Still smaller particles of gold, not visible with the ultramicroscope, can act as nuclei or centres of condensation for the production of ultramicroscopic particles; the diameter of these nuclei has been estimated at 10^{-7} cm. Zsigmondy, the inventor of the ultramicroscope, distinguished three kinds of small particles: *microns*, microscopically visible, diameter 10^{-3} to 10^{-5} cm. (in ordinary suspensions); *submicrons*, ultramicroscopically visible, diameter 10^{-5} to 5×10^{-7} cm. (in colloidal solutions); *amicrons*, invisible, but act as nuclei, diameter 10^{-7} cm. (in colloidal solutions).

If a few drops of eosin solution (red ink) are added to a trough of water, the path of a beam of light is made visible by a beautiful green light, not unlike the haze obtained with mastic, but coloured. With the ultramicroscope, however, no particles can be detected, and the effect is quite different from that shown by turbid liquids; it is known as **fluorescence**. The two effects are distinguished by the fact that light scattered from turbid media is polarised, whilst fluorescent light is not, or only slightly.

Solids may be produced in very thin films. Gold-leaf is only 10^{-5} cm. thick, and if a piece of burning magnesium ribbon is held behind a piece of gold-leaf pressed between two sheets of glass, the metal is seen to be translucent, and lets through a green light.

Smaller still than the colloidal particles are the **atoms and molecules**, which have diameters of the order of 10^{-8} cm. These are revealed when X-rays are used instead of ordinary light. X-rays differ from light only in having a much smaller wave-length, of the order of 10^{-8} cm., and if

they are allowed to fall on a crystal, the effect produced, although invisible, is similar to the colours seen with visible light falling on thin soap-films. The effect indicates that crystals are composed of layers of atoms, separated by distances of the order of 10^{-8} cm. (see Chapter XXIII).

The separation of mixtures of solids.—The phases of a mixture of solids may be separated in different ways.

(1) **Mechanically**, by picking out the different bodies, if the system is sufficiently coarse-grained.

(2) By differences of **density**. The powder is stirred with a liquid, the density of which lies between that of one of the solids and those of the others, and in which the solids do not dissolve. If powdered granite is shaken with a mixture of density 2.6, composed of benzene (density 0.879) and methylene iodide (density 3.33), the feldspar (density 2.57) will float, whilst the mica (density 2.85) and quartz (density 2.65) will sink. The two heavier minerals may be separated by another mixture of the liquids of density 2.7.

(3) By **magnetism**; iron filings are separated from flowers of sulphur by their attraction to a magnet, leaving the sulphur behind.

(4) By **electrification**; a mixture of red lead and washed and dried flowers of sulphur is dusted through muslin on to an ebonite plate rubbed with flannel: the positively charged red lead adheres to the negatively charged plate, whilst the sulphur, with the same charge as the plate, does not adhere. The plate is now tapped gently on a sheet of paper; the sulphur with a little red lead falls off, leaving the red lead on the plate; this may be brushed off on to the paper, and the colours of the two powders compared.

(5) By the different attractions of the solids for a liquid (**surface tension**); a mixture of powdered zinc blende (native zinc sulphide) and sand is sprinkled on the surface of water; the sand is wetted and sinks, but the blende is not wetted and floats, although it is heavier than water.

(6) By the different **solubilities** in a liquid; a mixture of iron filings and sulphur is shaken with carbon disulphide; the sulphur dissolves. The solution may be decanted from the iron, which is insoluble, poured into a dish, and the solvent allowed to evaporate, when crystals of sulphur are left.

(7) By **fusibility**; a mixture of lead shot and sand is heated in a crucible; the lead fuses and the sand floats to the top.

(8) By **volatility**; a mixture of sand and iodine is heated in a test-tube; the iodine forms a violet vapour, which condenses on the cool tube as a black crystalline **sublimate**, whilst the sand is left in the bottom of the tube.

The magnetic method separates the minerals *tinestone* (density 6.4–7.1) and *wolfram* (density 7.1–7.9), which occur together, and are so nearly alike in density that they cannot be separated by washing with a stream

of water. Tinstone is non-magnetic, whilst wolfram (an ore of tungsten, a metal used in making the filaments of electric lamps) is fairly magnetic. The crushed ore is dropped on a travelling belt passing over a magnetic

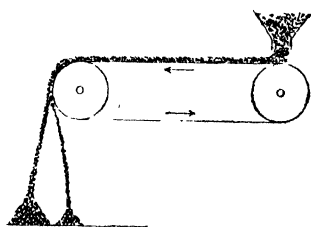


FIG. 4.—Electromagnetic separation (diagrammatic).

roller (Fig. 4), and falls off. The tinstone falls undeflected, but the wolfram is pulled towards the magnet, and forms a separate heap. The process is called **electromagnetic separation**.

Separation by surface tension is used in the **flotation process** for separating minerals such as zinc blende, not easily wetted by water, from galena (an ore of lead) which is. The crushed ore is agitated by a blast of air with water to which a little oil, e.g. of eucalyptus,

has been added. The blende forms a scum on the surface whilst the galena sinks.

The separation of solids from liquids.—Solids mixed with liquids may be separated in various ways.

(1) By settling out under the influence of gravity, *i.e.*, by **sedimentation**. The coarser the particles, the more rapidly they settle.

The velocity of settling of spherical solid or liquid particles, in a liquid or gas, is given by Stokes's equation :

$$c = \frac{2r^2g}{9\eta} (d - d') \quad \text{cm. per sec.}$$

where r = radius of the particles in cm. ; g = acceleration of gravity, 981 cm. per sec. per sec. ; η = viscosity of the liquid in c.g.s. units ; d and d' are the densities of the suspended particles and of the liquid, respectively. (If $d < d'$, the particles rise ; e.g. air bubbles in water.)

The rates of settling of particles of sulphur ($d = 2.06$) in water ($d = 1.00$; $\eta = 11.4 \times 10^{-3}$ at 15°), the diameters of the sulphur particles being 0.1 cm., and 0.0001 cm., as calculated from Stokes's formula, are 50 cm. per sec. and 0.00005 cm. per sec., respectively. The fine particles remain almost permanently in suspension, forming a colloidal solution.

Particles of different sizes mixed together may be separated by **fractional sedimentation** : the powder is stirred with water and the time of settling divided into a number of intervals. A series of powders increasing in fineness is obtained, and the process may be repeated.

(2) By **centrifugal force**.—A glass tube is filled with a fine suspension and placed in one of the metal containing-tubes of a centrifuge (Fig. 5), a similar tube of water being put in the opposite side as a counterpoise ; the powder is separated to the bottom of the tube on working the machine.

(3) The suspended particles may be electrically charged and move in an electric field ; this motion is called **electrophoresis** or **cataphoresis**.

A colloidal solution of arsenic sulphide is made by pouring a solution of arsenic trioxide in water into hydrogen sulphide solution, and driving out the excess of hydrogen sulphide by a stream of washed hydrogen. About 50 ml. of the yellow solution, with 5 gm. of urea dissolved in it to make it denser than water, are carefully run by a pipette into the lower part of a U-tube half-filled with distilled water. Platinum electrodes are placed in each arm of the tube and connected with the D.C. mains. The level of arsenic sulphide, marked by paper rings, falls on one side of the U-tube, and rises on the other (Fig. 6). The suspended particles in the colloidal solution give a Tyndall cone (p. 3).

(4) If a few drops of sulphuric acid are added to colloidal arsenic sulphide, precipitation in yellow flocks occurs. If the mixture is shaken with paraffin oil, the oil rises to the surface, carrying the arsenic sulphide with it. This is an application of **flotation**: arsenic sulphide adheres more strongly to oil than to water.

(5) The commonest method of separating solids from liquids is by **filtration**, usually through filter paper. Hot solutions filter more rapidly than cold ones, since the viscosity of the liquid is less at a higher temperature. The rate of filtration is also increased by increasing the difference of pressure between the two ends of the capillary pores of the filter (filtration under reduced pressure).

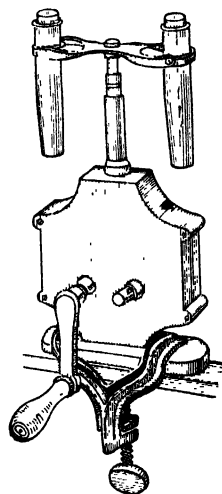


FIG. 5.—Centrifuge.

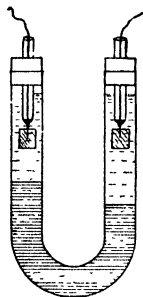


FIG. 6.—Electrophoresis.



FIG. 7.—Separating funnel.

The separation of liquids from liquids.—Chloroform and water shaken together in a **separating funnel** (Fig. 7), and allowed to stand, separate into two layers with the heavy chloroform below. This can be run off through the tap, leaving the water in the funnel.

A suspension of *fine* droplets of one liquid in another (such as milk) is called an **emulsion**. Each liquid alone may be transparent, but the

emulsion is turbid, owing to the scattering of light from the small drops, which have a different refractive index from that of the other liquid.

Emulsions can be separated in the centrifuge, or if one liquid is soluble in a third whilst the second is not, by shaking with the third liquid. If ether is shaken with an emulsion of paraffin oil and water the ether dissolves the paraffin and the solution floats to the surface.

The separation of gases from liquids and solids.—Gases mix in all proportions, so that heterogeneous systems can be obtained only when a light gas is stratified on a heavier one. The gases soon mix by diffusion.

Pass carbon dioxide into a large jar, so that the latter is partly filled with the gas (Fig. 8). Blow a soap bubble* and allow it to fall into the jar. It is arrested on reaching the carbon dioxide, and remains suspended. A lighted taper lowered into the jar is extinguished at the level of the bubble.

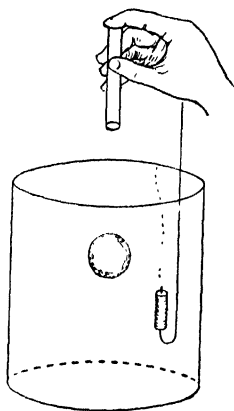


FIG. 8.—Experiment illustrating stratification of gases.

A suspension of minute bubbles of gas in a liquid is a froth or foam, and is usually produced by shaking the gas with a liquid of low surface-tension, such as soap solution. Froths may be separated by centrifugal force, or by adding other liquids, such as alcohol to aqueous foams.

A suspension of minute droplets of liquid in a gas, as produced by rapid cooling of moist air, is called a mist or fog. In fogs the particles are smaller, and a mist may pass over into rain when the particles coalesce into larger drops.

Aitken showed that mists are produced by condensation on minute solid particles (*notes*) of dust or (more probably) salt in air; if these are partly removed by filtering through cotton-wool, condensation on cooling occurs on the remaining nuclei, producing rain-like drops. If all nuclei are removed by allowing the air to stand in a vessel with wetted sides, condensation does not occur until the air is cooled much below the normal temperature of mist-formation. C. T. R. Wilson found that electrically charged nuclei (gaseous ions), produced even in dust-free air by electric sparks or exposure to X-rays, can act as condensation centres, and may also be filtered out by cotton-wool.

A suspension of fine solid particles in a gas is a smoke or fume. Coal smoke consists mainly of small particles of carbon, which aggregate to form soot. Smoke from the glowing tip of a cigarette, also consisting of small particles of carbon, appears blue because the particles are very fine, with diameters of the order of a wave-length of light. Smoke

* Plateau's Soap Solution is prepared as follows. 10 gm. of sodium oleate and 400 ml. of distilled water are allowed to stand at the ordinary temperature in a stoppered bottle until solution occurs. 100 ml. of pure glycerin are then added, and the liquid, after shaking, is allowed to settle for a few days in the dark. The clear liquid is decanted or siphoned off, and, after the addition of 1 drop of ammonia, is preserved in a stoppered bottle covered outside with opaque black varnish.

rising vertically from a chimney in clear dry air also appears blue, but smoke some distance from the end of a cigarette, or blown from the mouth, and smoke from a chimney on a damp day, appear greyish-white and opaque, because the particles are larger, probably as a result of the condensation of moisture upon them.

The particles in fogs and smokes may be electrically charged, or become so on exposure to a high-tension discharge from a point or wire attached to a pole of an electrical machine or induction coil. During such discharges the fume may precipitate, as was shown by Sir Oliver Lodge in 1883. This method of fume dissipation is applied to the precipitation of fumes from smelting furnaces, blast-furnaces, cement furnaces, etc.

Electrostatic precipitation is illustrated by the apparatus shown in Fig. 9. The bell-jar rests on a glass plate and the electrodes are copper plates soldered to copper wires fixed in the corks and connected with an induction coil. A small crucible contains cotton-wool moistened with concentrated ammonia solution and hydrogen chloride gas is passed in through the upper tube. A dense fog of ammonium chloride particles forms, but this rapidly settles upon the inside of the bell-jar when the induction coil is operated.

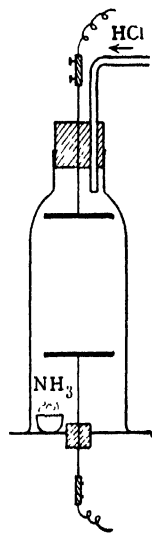


FIG. 9.—Electrostatic precipitation.

The Lodge-Cottrell apparatus consists of tubes or chambers containing electrodes, between which a high tension of 75,000 volts is maintained. The solid deposited from the fume passing through is shaken off the sides of the tube or chamber from time to time by tapping with an automatic hammer; liquids flow away without such treatment.

CHAPTER II

ELEMENTS, COMPOUNDS AND SOLUTIONS

Chemical changes.—Bodies often undergo very marked and permanent changes under certain conditions. Milk may become sour; bright copper becomes dull and ultimately covered with a green film when exposed to moist air, and under the same conditions iron rusts away completely to a brown powder. A candle burns away and apparently disappears. A piece of copper wire becomes covered with black scales when heated, and a piece of magnesium ribbon on heating in a bunsen flame takes fire and burns brilliantly, leaving a white ash.

In other cases the changes are less marked, and the properties of the materials are only slightly and temporarily modified. Water on cooling freezes to ice, but the ice melts and is reconverted into water on warming. A bar of iron which has been heated to redness is only slightly altered and, apart from a little scale on the surface, is recovered without change on cooling. A piece of platinum wire heated in a bunsen flame becomes red hot, but is unchanged on cooling.

Material changes either (i) alter only a few properties of the material and are temporary, when they are called **physical changes**; or (ii) they lead to a complete alteration of properties and the formation of a different material, when they are called **chemical changes** or **chemical reactions**.

The following experiments illustrate some striking chemical changes.

(1) A small piece of white phosphorus on a sand-tray is sprinkled with a few crystals of iodine. The phosphorus takes fire.

(2) Dilute solutions of potassium ferrocyanide, tannin, and potassium thiocyanate (all practically colourless) are poured into three glasses and a very dilute solution of ferric chloride acidified with a little hydrochloric acid (also practically colourless) is added. Blue, black, and red solutions are formed.

(3) A small pill of mercuric thiocyanate heated by the flame of a taper swells up into a worm-like mass of a friable yellow substance ("Pharaoh's Serpent").

(4) A mixture of 5 gm. of clean fine iron filings and 3 gm. of flowers of sulphur is heated in a test-tube. The mixture glows and continues to do so when taken from the flame. The change evolves a good deal of heat. When cold, the tube is broken in a mortar. A greyish mass is obtained, which is easily powdered. The powder is black, and under a lens no iron or sulphur particles can be seen in it, although these can be seen in the mixture. Carbon disulphide does not dissolve any sulphur from it (p. 5). If a

magnet is brought over it iron is not attracted, as it is from the mixture.* The iron and sulphur have disappeared as such and have formed a new substance, a chemical compound, iron sulphide.

From these experiments it is seen that chemical changes are often accompanied by an evolution of heat, when they are called **exothermic reactions**. This is not always the case, since in some chemical changes, called **endothermic reactions**, heat is absorbed.

(5) Concentrated hydrochloric acid is poured over crystals of Glauber's salt in a beaker; the crystals fall to a granular white powder of common salt and a considerable absorption of heat occurs, so that water in a small test-tube placed in the beaker is frozen.

Characteristics of physical and chemical changes.—Some of the main characteristics of physical and chemical changes may be summarised; the difference is sometimes not very marked.

I. **Physical changes**: no new substance is produced; if anything more than mere heating or cooling is involved, it is usually merely a change of state (melting, evaporation): apart from latent heat absorbed or evolved in changes of state, and heat supplied to or removed from a body, there is no marked evolution or absorption of heat; the change is easily reversed by appropriate alteration in the external conditions; the weight of the material remains unchanged.

II. **Chemical changes**: new substances with different properties are produced; there is usually evolution of heat (sometimes absorption of heat), and sometimes (as in combustion) of light; the change is not easily reversed by mere change of external conditions unless the system is in a state of equilibrium (see p. 162); the weight of a given material usually changes when it is converted into the new substance.

The law of conservation of mass.—The mass of a body, as determined by comparing its weight with that of standards by means of the ordinary balance, is generally regarded as a fixed property of the body.

Empedokles (490–430 B.C.) as quoted by Aristotle, says: "Nothing can be made out of nothing, and it is impossible to annihilate anything. All that happens in the world depends on a change of form and on the mixture or separation of bodies." This is similar to the statement of Lavoisier (1743–1794 A.D.), made over 2000 years later: "Nothing can be created, and in every process there is just as much substance (quantity of matter) present before and after the process has taken place. There is only a change or modification of the matter." Lavoisier's statement was founded upon experiment, and is called the **law of conservation of mass**.

* The powder is usually *feebly* magnetic as a whole. It may be noted as a curiosity that the composition of ferrous sulphide (nearly always given as the example of a chemical compound) is never exactly that given by the chemical formula FeS and is slightly variable; it always contains a little less iron than this formula indicates.

The early chemists ignored changes of weight in chemical processes, as removed from purely chemical studies and beneath notice. Jean Rey (1630) said: "The examination of weights by the balance differs from that made by the reason. The latter is only employed by the Judicious, whilst the former can be practised by the Veriest Clown. The latter is always exact, whilst the former is seldom without deception."

Joseph Black (1755) in a research on magnesia paid careful attention to the weights of the materials. "Three ounces of magnesia were distilled in a glass retort and receiver. When all was cool, I found only five drachms of whitish water in the receiver . . . the magnesia when taken out of the retort . . . had lost half its weight . . . It is evident that of the volatile parts contained in the powder, a small portion only is water; the rest cannot, it seems, be retained in vessels under a visible form . . . and is mostly *air* [carbon dioxide]." Black put down loss of weight in a chemical change to the escape of invisible material, thus recognising the principle stated later by Lavoisier. Black's experiment is an example of a chemical change in which an apparent destruction of matter is due to the escape of a gas. The fact that air, the only gas then known, has weight was proved by the following experiment of Otto von Guericke, the inventor of the air-pump (1654).

Exhaust by an air-pump, and counterpoise on the balance a 2-litre globe fitted with a stopcock (Fig. 10). Open the stopcock, notice the hissing noise of the air rushing into the globe, replace the globe on the balance, and notice that it has increased in weight.

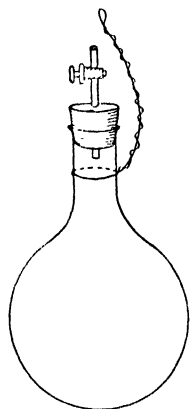


FIG. 10.—Flask for weighing air.

In order to test the truth of Lavoisier's principle the chemical change must be carried out in a closed vessel, so that no material used can escape.

Place a *small* piece of phosphorus, dried by pressing between filter paper, in a dry strong 250 ml. round-bottom flask fitted with a rubber stopper. Weigh the flask. Warm over a flame the spot where the phosphorus lies until the latter ignites. When combustion is finished, allow the flask to cool, and reweigh. The weight is unchanged.

Pour a little mercuric chloride solution into a conical flask, and place inside a small tube containing a solution of potassium iodide. Cork the flask and counterpoise on the balance. Now tilt the flask so that the solutions mix. A red precipitate of mercuric iodide is formed, but the weight will be found to be unchanged.

In 1900 Heydweiller stated that small losses of weight occurred when some chemical reactions were carried out in sealed vessels: 80 gm. of copper sulphate dissolved in 130 ml. of water were decomposed with 15 gm. of metallic iron, with a loss of weight of 0.217 mgm. H. Landolt in 1893-1908 carried out a series of experiments with the object of

determining whether the losses noticed were real, or due to some error of experiment.

In the separate legs of a Jona glass U-tube (Fig. 11) he sealed solutions of substances capable of reacting without the production of much heat, so that the disturbances arising from this cause could be eliminated. He used :

1. Silver sulphate and ferrous sulphate, giving a precipitate of metallic silver.
2. Hydriodic acid and iodic acid, giving a precipitate of iodine.
3. Iodine and sodium sulphite, giving sodium iodide and sulphate.
4. Chloral hydrate and potassium hydroxide, giving an emulsion of chloroform.

The tube was counterpoised against an exactly similar tube on a balance capable (in the final experiments) of detecting a change of weight of 0.0001 gm. with a load of 1 kgm. in each pan, *i.e.* a change of 1 part in 10,000,000. One reaction tube was inverted, after removing from the balance, and the chemical change allowed to take place. After cooling, the tube was replaced on the balance and the change in weight, usually a diminution, noted. The other tube was then taken off the balance and inverted, and the process repeated.

At first, slight losses in weight, 0.167 mgm. in the maximum, were always found, but after a long series of experiments these were traced to two causes:

(a) as a result of the slight evolution of heat, the film of moisture condensed on the outer surface of the glass was partly driven off, and did not return until after long standing ;

(b) the vessel expanded slightly as a result of the slight increase of temperature, and did not return to its original volume until some time had elapsed.

In consequence of the first error the weight of the vessel was reduced, and the second error, which led to an increase in volume of air displaced by the vessel, also reduced the apparent weight. By allowing the vessel to stand for a long time before reweighing, Landolt found that it recovered its original weight to within 1 part in 10,000,000—*i.e.* within the limits of experimental error. By using silica tubes (which do not expand) covered with wax (to prevent the formation of a film of moisture), no change in weight was observed within the same limits of error.

Experiments by Manley (1912) with the reaction between barium chloride and sodium sulphate solutions, giving a precipitate of barium sulphate, showed that the weight remained constant to 1 part in 100,000,000. In all ordinary chemical experiments, the law of conservation of mass is exact.

According to the Theory of Relativity, the absolute energy E of a mass m is $E = mc^2$, where c is the velocity of light. A chemical change attended by a loss of energy ΔE will give rise to a loss of mass $\Delta m = \Delta E/c^2$. Since c is very large this will be quite negligible in ordinary reactions : to produce a loss of 1 mgm. would require the combustion of $3\frac{1}{2}$ tons of phosphorus.

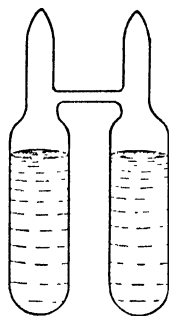


FIG. 11.—Landolt's experiment.

In radioactive changes, which are attended by very large energy changes relative to the masses involved, the changes of mass are appreciable (see Chapter XXIII).

Elements and compounds.—A homogeneous material may undergo complete chemical change in one of three ways, according to its composition. The substance may *increase in weight* in all the changes, when it *combines* with other substances; or it may give other substances, each of smaller weight than the original substance, or *decomposes* into these; or its weight may remain the same. The third case (*isomeric* or *allotropic change*) is considered later.

Heat 0.5 gm. of magnesium ribbon in a weighed, loosely closed, porcelain crucible, with a small flame till combustion ceases (Fig. 12). Then heat strongly for a few minutes with the lid off, cool and reweigh. Repeat until the weight is constant. There is an *increase in weight* of a little over 0.3 gm.

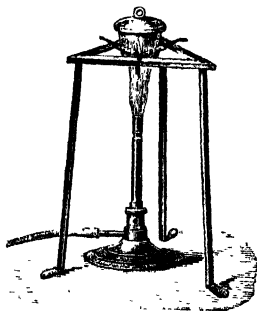


FIG. 12.—Heating magnesium in air.

Heat 2.16 gm. of red oxide of mercury in a weighed, hard glass tube, with a glass delivery tube leading to a pneumatic trough in which is inverted a measuring cylinder full of water (Fig. 13). The red substance blackens and bubbles of gas collect in the cylinder. At the same time a sublimate of mercury collects on the cool part of the tube. When evolution of gas ceases and the oxide has disappeared, remove the delivery tube from the trough and allow the apparatus to cool. Reweigh the tube. The

loss in weight of the tube should amount to 0.16 gm. The volume of gas collected will be about 118 ml. A glowing chip of wood is rekindled in the gas, which is oxygen.

If a pure substance can be decomposed into two or more substances each of smaller weight, as the oxide of mercury into mercury and oxygen, it is said to be a **compound**. If it always yields substances of greater weight, indicating that union occurs with other substances, the substance is called an **element**. Magnesium is an element. A substance which does not alter in weight after undergoing *chemical* change may be either an element or a compound.

Pure substances and solutions.—At this point we meet a difficulty, viz. that in some cases a homogeneous material has a continuous range of compositions. Solutions of common salt in water at 0° may vary in composition from pure water to a solution containing 26.5 per cent by weight of salt. Between these two limits there is an infinite number of compositions. But if we decompose oxide of mercury, no matter how it has been prepared, we find that it always has the same composition, containing 8 gm. of oxygen to 100 gm. of mercury.

We therefore divide all homogeneous materials which are not elements into two classes. Those of constant composition are called **compounds**, those of variable composition are called **solutions**. Oxide of mercury is a compound, liquids containing salt and water are solutions.

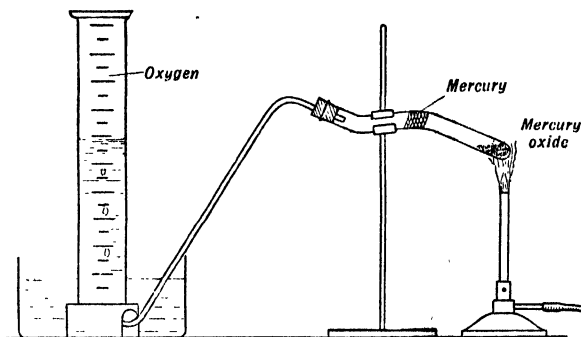
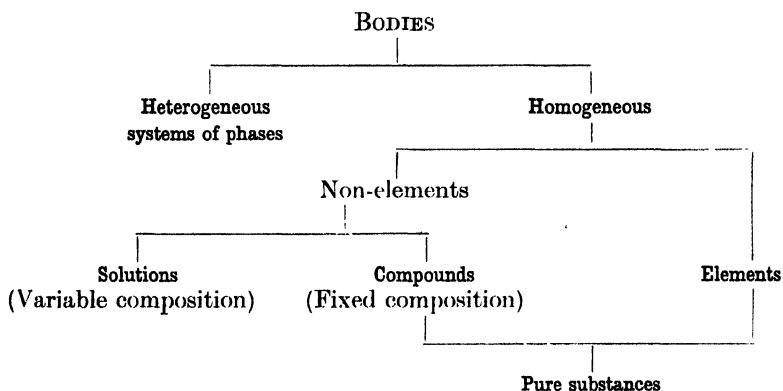


FIG. 13.—Decomposition of mercuric oxide by heat.

A solution is always separable by suitable means into two or more pure substances, either elements or compounds. Solutions of salt in water are separated into salt and water by simple evaporation. The solutions of salt and water are not put in separate groups of substances, but are regarded as solutions of *two* pure substances (salt and water) in varying proportions.

We have arrived at the following classification :



Analysis and synthesis.—The process by which a compound is separated into its elements is called **analysis** (from the Greek *analuo*, I unloose). The formation of a compound from its elements is called **synthesis** (the Greek word *synthesis* meaning a putting together). The process of finding the composition of substances is also called analysis; **qualitative analysis** leads to a knowledge of the constituents only, whilst **quantitative analysis** determines the proportions in which they are united.

Compounds.—It follows from the definition of a compound that its composition is independent of the method of preparation, and that the same compound gives the same elements in the same proportions in its decomposition.

Metallic tin may be converted into oxide of tin in three different ways :

(a) One gm. of tin is weighed into a counterpoised Rose's crucible (Fig. 14), and heated in a stream of oxygen passed through the porcelain tube in the crucible lid. The crucible is cooled and weighed from time to time until its weight becomes constant. The residue is oxide of tin.

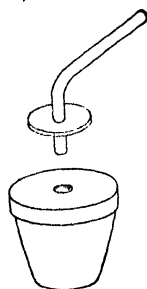


Fig. 14.—Rose's crucible.

(b) One gm. of tin foil is weighed into a counterpoised porcelain basin, covered with a large watch-glass. It is treated carefully with successive small amounts of concentrated nitric acid until the violent action ceases, the watch-glass being placed over the basin after each addition to prevent loss by spirting. The excess of acid is evaporated off on a sand-bath, and the dry material heated for a few minutes over a Bunsen flame. The dish is cooled and weighed. The residue is oxide of tin.

(c) One gm. of tin is weighed into a conical flask and dissolved in hydrochloric acid by warming. The solution of chloride of tin is diluted with water, and precipitated with a stream of hydrogen sulphide. The tin sulphide is filtered and washed, the filter paper and precipitate ignited in a weighed porcelain crucible, cooled and weighed. The residue is oxide of tin.

Within the limits of experimental error the weight of oxide of tin obtained from 1 gm. of tin in the three different methods is the same. The composition of oxide of tin is constant, and independent of the method of preparation. Oxide of tin is a compound, not a mixture or a solution.

The chemical elements.—About ninety elements occur in nature (see the list inside the front cover). Of these about one-half are commonly found in chemical laboratories, and of these about twenty occur in nature in the uncombined state. About 99 per cent. of terrestrial bodies are composed of some twenty elements and their compounds.

An estimate of the occurrence of the elements in the air, the sea and other waters, and the crust of the earth to a depth of twenty-four miles, has been made by F. W. Clarke, and in meteorites (318 iron and 125 stone) by O. C. Farrington. The table on p. 17 (for the symbols see inside front cover) gives the average composition by weight of these materials in parts per 100.

A combined table for the terrestrial distribution is the following, due to Clarke :

Oxygen	-	49.85	Calcium	-	3.18	Hydrogen	-	0.97
Silicon	-	26.03	Sodium	-	2.33	Titanium	-	0.41
Aluminium	-	7.28	Potassium	-	2.33	Chlorine	-	0.20
Iron	-	4.12	Magnesium	-	2.11	Carbon	-	0.19

Oxygen is seen (Fig. 15) to be the most abundant element, accounting for one-half the total mass ; silicon, which occurs mainly in the form of

DISTRIBUTION OF THE ELEMENTS.

Lithosphere.	Hydrosphere.	Atmosphere.	Meteorites.
O - - 47.33	O - - 85.79	N - - 75.53	Fe - - 72.06
Si - - 27.74	H - - 10.67	O - - 23.02	O - - 10.10
Al - - 7.85	Cl - - 2.07	A - - 1.40	Ni - - 6.50
Fe - - 4.50	Na - - 1.14	H - - 0.02	Si - - 5.20
Ca - - 3.47	Mg - - 0.14	C - - 0.01	Mg - - 3.80
Na - - 2.46	Ca - - 0.05	Remainder 0.02	S - - 0.49
K - - 2.46	S - - 0.05	—	Ca - - 0.46
Mg - - 2.24	K - - 0.04	—	Co - - 0.44
Ti - - 0.46	N - - 0.02	—	Al - - 0.39
H - - 0.22	Br - - 0.01	—	Na - - 0.17
C - - 0.19	C - - 0.01	—	P - - 0.14
P - - 0.12	I - - 0.006	—	Cr - - 0.09
S - - 0.12	Fe - - 0.002	—	C - - 0.04
Mn - - 0.08	Remainder 0.002	—	K - - 0.04
Ba - - 0.08	—	—	Mn - - 0.03
F - - 0.07	—	—	Ti - - 0.01
Cl - - 0.06	—	—	Cu - - 0.01
N - - 0.02	—	—	Remainder 0.03
Sr - - 0.02	—	—	—
Remainder 0.51	—	—	—
100.00	100.00	100.00	100.00

the oxide silica as quartz and sand, and in combination in many rocks, is next in abundance. Nitrogen, contained in the atmosphere, and

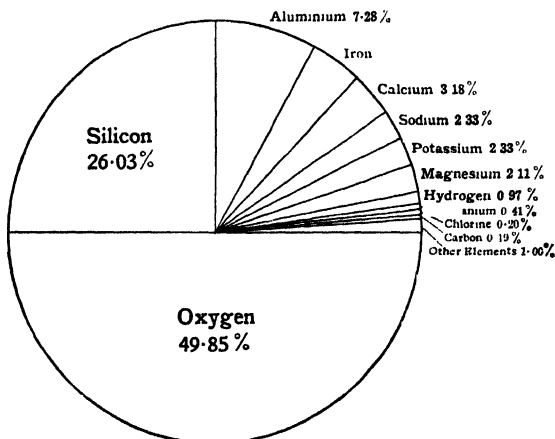


FIG. 15. —The distribution of the elements.

other elements, especially carbon, contained in all living matter, together equal only about 1 per cent. of the whole.

The composition of the centre of the earth is not accessible to experiment, but since the mean density of the earth is about 5.6, the core must consist largely of substances of high density, probably iron with some nickel. This is surrounded by an intermediate shell of sulphides and oxides, or perhaps oxides only, of the heavier metals, and this in turn is enclosed by an outer shell of silicates.

By spectrum analysis (Chapter XXXVI) it is possible to discover the elements present in the sun and stars. About one-half the number of terrestrial elements have been identified in them, and there is no reason to believe that any are absent.

The four elements.—The conceptions underlying the definitions of elements and compounds, although now almost obvious, were reached only after centuries of effort. A brief account of the development of these fundamental conceptions will now be given.*

The first clear expression of the idea of an element occurs in the teachings of Greek philosophers, beginning with Thales (640–546 B.C.) who taught that all things arose from *water*. Anaximenes (560–500 B.C.) thought *air* was the primary substance, whilst Herakleitos (536–470 B.C.), impressed by the constant change of the material world, regarded the ever-varying *fire* as the fundamental principle. Empedokles (490–430 B.C.) introduced the ideas of four “roots” of things: fire, air, water and earth, and two forces, attraction and repulsion, which joined and separated them. Aristotle (384–322 B.C.) summarised the earlier

theories and developed the idea of a primary matter, called *hylé*, on which a specific form (*eidos*) could be impressed. The same primary matter can receive different forms, just as a sculptor can make different statues from the same block of marble, although Aristotle preferred to think of the form as evolving from within, as in organic growth. The forms can be removed, and replaced by new ones, so that the idea of transmutation of elements arose. Aristotle's elements are really fundamental properties of matter, for

FIG. 16.—Aristotle's four elements.

which he chose hotness, coldness, moistness, and dryness. By combining these in pairs, as in the diagram, he obtained the four elements, fire, air, water, and earth.

Water is the type of moist and cold things, fire of hot and dry, and so on. To the four material elements a fifth immaterial one was added, which appears in Aristotle's later writings as the *quintessence* or the *ether*.

The early history of chemistry.—Chemistry had its origin about the beginning of the Christian era in the Hellenistic-Egyptian city of Alexandria, and was the result of the blending together of knowledge

* See the author's *Short History of Chemistry* (Macmillan) for further details.

from two sources : (1) the speculative philosophy of Greece, and (2) the Egyptian practical arts of working in metals and glass, and dyeing. The Egyptian technique, handed down in the workshops, is described in the *Papyrus of Leyden*, written in Greek about 300 A.D., although probably derived from older Egyptian sources. Some materials described are given Egyptian names (*e.g. asem* for an alloy of gold and silver). The papyrus seems to have included the working notes of a fraudulent goldsmith. Recipes for *plating* base metals with gold occur in it, but the author is aware that transmutation did not occur. Thus, he says :

“ One powders up gold and lead into a powder as fine as flour, 2 parts of lead for 1 of gold, and having mixed them, works them up with gum. One covers a copper ring with the mixture ; then heats. One repeats several times until the object has taken the colour. It is difficult to detect the fraud, since the touchstone gives the mark of true gold. The heat consumes the lead but not the gold.”

The earliest of the true chemical treatises, written in Greek at Alexandria during the first four centuries A.D., already speak of the *artificial*

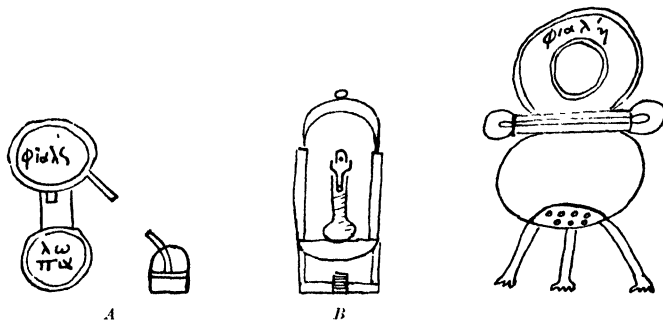


FIG. 17.—Illustrations of chemical apparatus copied from Greek MSS. of Zosimos and others in the Bibliothèque Nationale, Paris. A represents apparatus for distillation, later called alembic : in the MSS. the lower part is called *lopas*, the upper *phiale* C, is a brazier, or *kerotakis* ; B an apparatus for heating a phial in a sand bath. All this apparatus was well known before 300 A.D.

production of gold and silver and the imitation of valuable dyes. The earliest name for chemistry is the *Divine Art* ; the name *chemeia* appears about 250 A.D. and seems to be derived from the Egyptian word *chemi*, meaning “ black,” or “ Egyptian,” or both. One of the earliest treatises is attributed to Demokritos, but is not written by Demokritos of Abdera (*c.* 500 B.C.), a famous natural philosopher and one of the originators of the atomic theory (p. 92), but during the first century A.D. The most considerable treatise is by Zosimos of Panopolis in Egypt, who lived about 250–300 A.D., and used the name *chemeia*. These treatises contain descriptions of chemical apparatus (Fig. 17), especially for distillation, of many chemical operations, and of some substances not mentioned by earlier authors, such as Pliny, Dioskourides and Galen.

Alchemy.—In 640 A.D. Egypt was conquered by the Arabs, who caused translations of Greek works on medicine and chemistry to be made by Nestorian Christians, these translations often going through the stage of Syriac. The Arabic name *alchemy* is the Greek-Egyptian *chemica* with the Arabic definite article *al* prefixed.

Chemistry among the Arabs was principally cultivated by Jābir ibn Hayyān (c. 721-817 A.D.) and al-Rāzī ("Rhazes") (d. 925 A.D.). Jābir and Rhazes were skilled practical chemists; ibn Sina ("Avicenna")

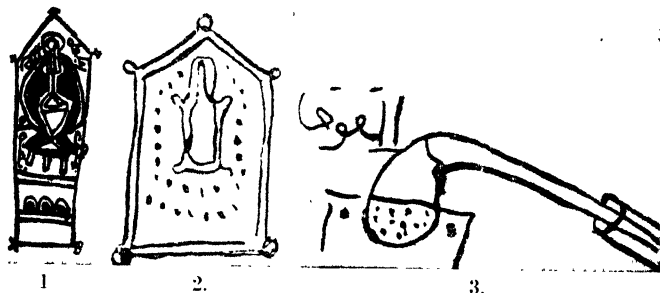


FIG. 18 — (1) Apparatus for digestion (Syriac MS). (2) Apparatus for digestion in small chamber (Syriac MS). (3) Retort and receiver (Syriac MS) a later addition.

(b. 980 A.D.) probably did not make chemical experiments, but was credited with a book on alchemy quoted by Roger Bacon. Jābir taught that metals are composed of mercury and sulphur, and are generated in the interior of the earth from these materials.

A knowledge of chemistry came to Europe in translations of Arabic works made in Spain, beginning about 1100 A.D., and important early students of the subject were Albertus Magnus (1193-1260) in Germany, Roger Bacon (1214-1292) in England, Raymond Lully (1235-1312 ?) in Spain, and Arnold of Villanova in Spain or France (1240-1319). The great minds soon lost interest in the subject, since the supposed transmutations of base metals into gold were found to be fraudulent.

The three alchemical elements (*tria prima*): salt, sulphur and mercury, were introduced by Paracelsus (1493-1541); sulphur was the principle of combustibility, salt the fixed part left after calcination, whilst mercury was the principle of metallicity, contained in all metals.

It was supposed that the base metals could be converted into gold and silver by altering the proportions of mercury and sulphur in them and "cleansing" the latter. This process was to be brought about by the *philosopher's stone*, described as red powder. Some recipes for its preparation, in so far as they are intelligible, show that it was a compound of gold, or a solution of gold in mercury, the latter being driven off in the fire, leaving the gold.

Experiments on supposed transmutation included roasting the sub-metallic mineral galena in air, when lead was formed, with a strong smell of sulphur, and the production of a small button of silver when the lead was burnt off by heating on a cupel, or dish made of bone-ash. Iron pyrites, a yellow mineral looking somewhat like gold, was melted with lead and the

lead cupelled, when a minute amount of gold was left. Both the silver and gold pre-existed in the minerals, and are separated from them at the present day. A steel knife-blade dipped into a solution of blue vitriol (copper sulphate) apparently became converted into copper.

The later history of alchemy contains records of frauds. One method was to stir the materials in a crucible with a hollow iron rod filled with gold powder, and stopped with wax. Many alchemists, however, were honest, and in making experiments they added useful knowledge to practical chemistry.

Iatrochemistry.—About 1500 another school of chemists arose, the **Iatrochemists**, *i.e.* medical chemists, who attempted to prepare the *elixir of life* which should cure all diseases and confer perpetual youth. Paracelsus (1493–1541) was the founder, and he also believed in the philosopher's stone.

Van Helmont (1579–1644) represents the transition from alchemy to modern chemistry. His writings show the beginnings of scientific method, although he still believed in transmutation, and sought the *alkahest* or universal solvent. He thought everything was derived from water, as taught by Thales, and describes an experiment in which a small willow twig was grown in a weighed pot of earth, supplied only with water. After five years the tree was weighed, and had gained 164 lb. in weight, the earth having lost practically nothing. Hence he concluded that the tree had been formed solely from water.

It is an irony of fate that this conclusion, in which the assimilation of carbon dioxide from the air by the plant was ignored, was reached by the discoverer of that gas. Van Helmont invented the name *gas*, derived from *chaos*, describing the supposed wild motion of its particles, and called carbon dioxide *gas sylvestre*, *i.e.* the "gas of the woods" or the "wild, untamable gas," because, having corked up limestone and acid in a bottle, he found that the latter was burst by the gas sylvestre. A gas, according to him, is something which cannot be kept in a vessel.* In his treatise "de Flatibus" he mentions another gas, *gas pingue*, which is inflammable and is produced in putrefaction. It was probably impure hydrogen.

Robert Boyle.—Modern chemistry may be said to have begun with Robert Boyle (1627–1691), and for two reasons. In the first place Boyle was the first to study chemistry for its own sake, and not as a means of making gold or medicines. In the second place, he introduced a rigorous experimental method into chemistry, and in particular overthrew the doctrines of the Aristotelian and Alchemical elements, by showing that none of them could by any process be extracted from metals. In the case of gold, neither water nor solvents can extract sulphur or mercury from it: the metal may be added to, and so brought into solution or crystalline compounds, but the gold particles are present all the time, and the metal may be reduced to the same weight of yellow, malleable, ponderous substance as it was before its mixture.

* "Hunc spiritum incognitum hactenus, novo nomine *gas* voco, qui nec vasis cogi, nec in corpus visibilo reduci potest nisi prius extincto semine."

Boyle in his *Sceptical Chymist** (1661), agreed to use "elements and principles as terms equivalent, and to understand both by the one and the other, those primitive and simple bodies of which the mixed ones are said to be composed, and into which they are ultimately resolved". According to Boyle, the elements are the practical limits of chemical analysis. Lavoisier, in his *Traité de Chimie* (1789), adopted the same



ROBERT BOYLE.

definition, at the same time emphasising that at some future date, with improved methods, substances then regarded as elements might be shown to be compounds, although "we ought never to suppose them compounded until experiment and observation have proved them to be so".

Lavoisier was also the first to give a nearly correct, though incomplete, table of chemical elements. Some substances which he classed as elements, such as the so-called "earths" (lime, magnesia, alumina) and the alkalis (potash, soda), were afterwards shown by Davy to be compounds (as Lavoisier suspected), and many elements have been discovered since Lavoisier's time.

* Reprinted in the *Everyman* series.

Chemistry had a long road to travel between the times of Boyle and Lavoisier, and at times went astray. This was particularly the case in the study of combustion, in which after a good start with Boyle, Hooke, and Mayow, a false turn was taken with the so-called phlogiston theory. It was the establishment of the true theory of combustion by Lavoisier, and the discovery of the composition of water by Cavendish, which laid the foundations of modern chemistry. These two aspects of the subject will be taken up in the chapters which follow.

CHAPTER III

THE COMPOSITION OF THE AIR AND THE THEORY OF COMBUSTION

The discovery of gases.—Reference has been made to the two gases described by Van Helmont (c. 1620), *gas sylvestre* (carbon dioxide) and *gas pingue* (hydrogen). Stephen Hales (1727) collected several gases over water, but did not realise their qualitative differences. The two gases of Van Helmont were carefully investigated by Henry Cavendish (1766); *gas sylvestre* was named *fixed air* by Joseph Black (1754), and *gas pingue inflammable air* by Cavendish (1766). Inflammable air was obtained by the action of sulphuric and hydrochloric acids on zinc, iron, and tin. Cavendish observed that the inflammable air was “the same, and of the same amount, whichever acid is used to dissolve the same weight of either metal,” iron and zinc, and hence he concluded that it came from the metal. Inflammable air was much lighter than common air, whilst carbon dioxide was heavier. He collected fixed air over mercury and determined its solubility in water. (“On Factitious Airs,” *Phil. Trans.*, 1766.)

Joseph Priestley (1733–1804),* discovered several new gases. At that time gases were called “airs,” Van Helmont’s name gas having dropped out of use. Priestley prepared and examined oxygen, nitrous oxide, nitric oxide, nitrogen dioxide, hydrogen chloride, ammonia, silicon fluoride, and sulphur dioxide. He improved the pneumatic trough, and collected over mercury many gases which are very soluble in water (e.g. ammonia, and sulphur dioxide). Priestley’s work established the existence of different gases each with definite properties.

Combustion and the calcination of metals.—There are two kinds of chemical change which, since they were investigated side by side and depend on the same cause, may be described together. These are combustion, and the calcination of metals.

The alchemists attached importance to the effects of heat on substances. Metals, except gold and silver, change when heated in open crucibles, and leave a dross, which was called a *calx* (Latin *calx*, lime). It was noticed in the sixteenth century that this *calx* is heavier than the metal: the explanation usually given was that fire has weight, and was absorbed by the metal in forming the *calx*. Jean Rey (1630) “devoted several hours to the question”, without making many experiments, and concluded that the air becomes thickened or adhesive by the action of the fire, and mixes with the *calx*.

* *Observations on Different Kinds of Air*, 6 vols. 1774–86; abridged edition, 3 vols. 1790.

Nitre air.—Robert Boyle * (1673) heated tin in a glass retort, and when it was melted sealed off the neck and continued the heating for two hours. The retort was cooled and the sealed tip of the neck broken. Air rushed in, “because when the retort was sealed, the air within it was highly rarefied.” Boyle, from his method of experimenting, did not notice (as Lavoisier did a century later) that some of the air was absorbed, although he found that the tin had increased in weight.

Boyle showed that sulphur sprinkled on a red-hot plate under an exhausted air-pump receiver smoked but did not burn. On admitting air, “divers little flashes were seen.” But if gunpowder were sprinkled on the hot plate under the vacuum receiver he saw “a pretty broad blue flame, like that of brimstone, which lasted so long as we could not but wonder at it.” Gunpowder could also burn under water. Boyle, somewhat reluctantly, concluded that a flame can exist without air, and that the increase in weight of metals on calcination is due to their absorption of “igneous corpuscles,” which he considered to be material and capable of being weighed in a balance. He observed that if charcoal is strongly heated in a closed retort it does not burn, but the *caput mortuum* (a fanciful name due to the alchemists, who represented a residue by the symbol of the skull and crossbones) becomes black again on cooling. If air is admitted the charcoal burns and crumbles to white ashes.

The last experiment was repeated by Robert Hooke (at one time an assistant to Boyle), who in his *Micrographia* (1665) put forward the first rational theory of combustion. Hooke found that a bit of charcoal or sulphur burns brilliantly when thrown into fused nitre.

Fuse about 5 gm. of nitre in each of two hard-glass test-tubes, supported by clamps over a tray of sand. Throw into one a small piece of charcoal; this swims about and burns brightly. Into the other throw a *small* piece of sulphur; this burns with a blue flame.

On the basis of experiments (not published) Hooke founded his theory of combustion:

“(1) Air is the universal dissolvent of all sulphurous (*i.e.* combustible) bodies. (2) This action of dissolution produces a very great heat, and that which we call *fire*. (3) This dissolution is made by a substance inherent and mixed with the air that is like, if not the very same with, that which is fixed in saltpetre (nitre).” He called this part of the atmosphere “nitrous air” (or nitre air). In this way he was able to explain the combustion of gunpowder, one constituent of which is nitre, in the absence of air.

John Mayow † (1641–1679) elaborated a theory similar to Hooke’s but supported by descriptions of experiments. He concluded that air consists of two gases; one is the nitrous air of Hooke, called by Mayow the nitro-aerial spirit (*spiritus nitro-aereus*), which is concerned in combustion and respiration, and the other is an air incapable of supporting either of the latter.

* *Works*, edited by Birch, 5 vols. 1744; abridged by Boulton, 4 vols. 1699–1700; do. by Shaw, 3 vols. 1725.

† *Tractatus quinque medico-physici*, Oxford, 1674.

(1) Mayow inverted a glass globe over a lighted candle standing in water, equalising the levels of the water by a siphon, which was then quickly withdrawn. The water rose inside the globe, showing that some air had disappeared. When the candle was extinguished, a large bulk of air was left, but this would not support the combustion of sulphur or camphor on a small sholf inside the globe when they were heated by a burning glass. (Fig. 19).

(2) A mouse introduced into a vessel together with a burning lamp lived only half as long as a mouse in the same vessel without the lamp. If a mouse was kept in a vessel of air closed by a bladder (Fig. 19), the contraction of the air was perceptible.

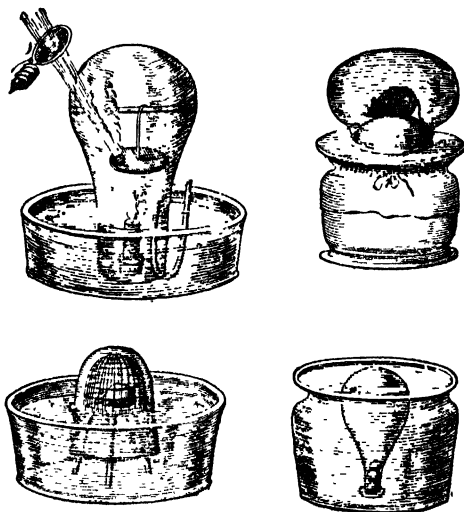


FIG. 19.—Mayow's experiments (from his *Tractatus quinque medico-physici*, 1674).

The illustrations depict the experiments on combustion and on the respiration of a mouse described in the text; also the contraction of air confined over water by the respiration of a mouse, and the collection of "air" (nitric oxide) from iron balls and dilute nitric acid in an inverted flask.

(3) Gunpowder rammed into a paper tube and ignited continued to burn under water. The air fixed in nitre can therefore take the place of ordinary air in supporting combustion, and since things burn more brilliantly in fused nitre than in common air, the nitre must contain an abundant supply of nitre air, which is the part of common air concerned in combustion.

(4) Mayow refers to an experiment described by Hamerus Poppius (1625) and Le Fevre (1660), viz. calcining metallic antimony on a marble slab by means of a burning-glass. Although abundant fumes were evolved, the calx weighed more than the metal. The calx was identical with that formed by the action of nitric acid on the metal.

Mayow did not succeed in isolating nitrous air, although but a step was

needed, viz. strongly heating nitre, and although Hooke in his *Lampas* (1677) says that his theory was generally received (a similar theory was, in fact, mentioned by Lemery in his *Cours de Chymie*, 1675), these beginnings of a true theory of combustion gave place to a theory due to two German chemists, which persisted for a century and obscured nearly every branch of chemical science. This was the famous phlogiston theory of Becher and Stahl.

The phlogiston theory.—John Joachim Becher in his *Physicæ subterraneæ* (1669) remarked that the constituents of bodies are air, water, and three earths, one of which is *inflammable* (*terra pinguis*), the second *mercurial*, the third fusible or *vitreous*. These correspond with the sulphur, mercury, and salt of the alchemists.

Georg Ernst Stahl, professor at Halle, in his lectures and text-book (*Fundamenta chymiae*, 1723) popularised and improved Becher's views. He used the name phlogiston (from the Greek *phlox* = flame) for the *terra pinguis*. When bodies burn, phlogiston escapes with a rapid whirling motion; when the original bodies are recovered by reduction, phlogiston is replaced. Oil, wax, and charcoal are rich in phlogiston, and may restore it to a burnt material. Zinc on heating in air burns with a brilliant flame, hence phlogiston (ϕ) escapes. When the white calx of zinc formed is heated with charcoal (rich in phlogiston), zinc distils: calx of zinc + ϕ = zinc. Similarly with other metals. Phosphorus burns to produce an acid and much heat and light are evolved: phosphorus = acid + ϕ . If the acid is heated with charcoal, phlogiston is absorbed and phosphorus is reproduced.

Stahl's theory united many previously isolated facts, and was largely accepted during the eighteenth century, although Boerhaave, in his important *Elementa Chymiae* (1732), does not mention it. During this period the increase in weight of metals on calcination was usually ignored, although the fact was destined later to overturn the phlogiston theory.

This increase of weight is shown by experiment. Finely divided *reduced iron* is taken up by a horse-shoe magnet counterpoised from a balance (Fig. 20), a piece of asbestos paper being placed in the pan underneath. A spirit-lamp flame is applied to the tufts of iron; the powder begins to glow, and after calcination falls from the magnet. The pan on the side of the magnet sinks, because the iron increases in weight.

Scheele's experiments.—Carl Wilhelm Scheele (1742–1786), a poor apothecary in Sweden, made a great number of fundamental chemical discoveries, those on combustion being published in his treatise *On Air and Fire*. The experiments were nearly all made before 1773 but owing to delay the book did not appear until 1777, when many of Scheele's discoveries had been made independently, and published, by Priestley in England. Scheele's priority was established in 1892 from his original laboratory notes.

In his first set of experiments Scheele measured the contraction of air standing in contact with a solution of liver of sulphur (*hepar sulphuris*), a solution of sulphur in lime-water, linseed oil, and iron filings moistened

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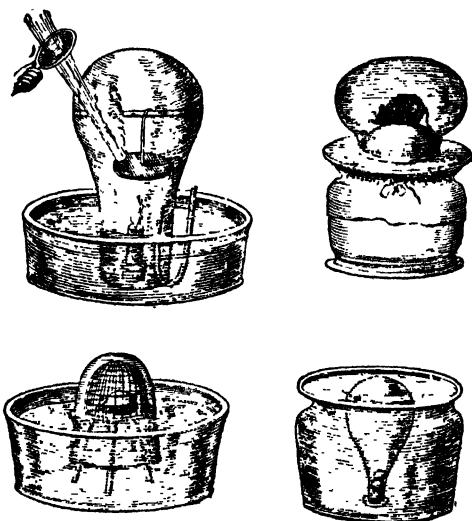


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In his first set of experiments Scheele measured the contraction of air standing in contact with a solution of liver of sulphur (*hepar sulphuris*), a solution of sulphur in lime-water, linseed oil, and iron filings moistened

with water, all of which, he says, are rich in phlogiston or the *inflammable substance*. In all cases there was a loss of air. A yellow solution

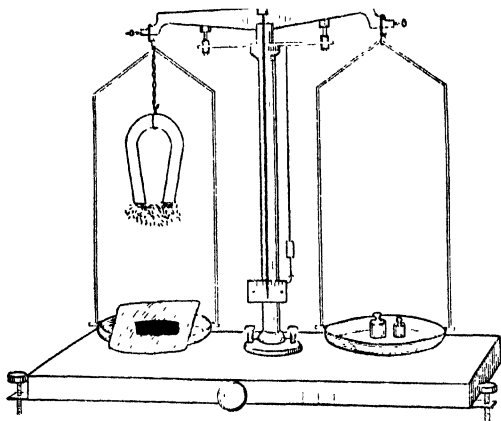


FIG. 20.—Increase in weight of iron on burning.

of sulphur in potash became colourless in contact with air, and then contained “vitriolated tartar,” which could be formed from potash and sulphuric acid.

Take three glass tubes, 2 ft. long and $\frac{3}{4}$ in. wide, fitted with rubber stoppers and divided into five equal volumes by strips of label. In one place a moistened piece of liver of sulphur (made by fusing potassium carbonate with flowers of sulphur in a covered crucible till evolution of gas ceases), and in a second a piece of phosphorus stuck on a piece of copper wire. Wet the inside of the third tube with water and sprinkle it with clean iron filings. Allow the three tubes to stand inverted in a cylinder of water for a few days (Fig. 21) and observe that the water rises in the tubes until one-fifth of the volume is occupied. Cork the tubes, remove them and insert a lighted taper into each. The flame is extinguished.

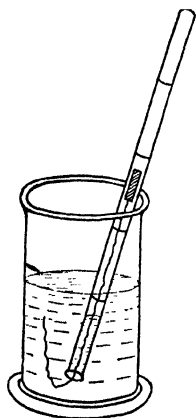


FIG. 21.—Diminution of air by phosphorus.

The inflammable substance was not in the residual gas, for if this had been formed by the union of common air with phlogiston, and contraction, it should be denser than common air. But: “a very thin flask which was filled with this air, and most accurately weighed, not only did not counterpoise an equal volume of ordinary air, but was even somewhat lighter.”

Thus, “the air is composed of two fluids, differing from each other, one of which does not manifest in the least the property of attracting phlogiston, whilst the other, which composes between the third and

fourth part (really one-fifth) of the whole mass of the air, is peculiarly disposed to such attraction." These two fluids Scheele called *foul air*, and *fire air*, respectively.

Scheele next placed a little phosphorus in a thin flask, corked the flask, and warmed it until the phosphorus took fire. A white cloud was produced, which attached itself to the sides of the flask in white flowers of "dry acid of phosphorus." On opening the flask under water, the latter entered and occupied a little less than one-third of the flask. By allowing phosphorus to stand for six weeks in the same flask until it no longer glowed, contraction of the air also occurred.

Scheele then burned a hydrogen flame in air in a glass globe standing over water (Fig. 22). The water rose until it filled about one-fourth of the flask, when the flame went out.

Burn a jet of hydrogen from a Kipp's apparatus inside a graduated boll-jar over water. The gas is turned off as soon as the flame (which becomes enlarged and very dim towards the end) goes out. After cooling, one-fifth of the air has disappeared (Fig. 23).

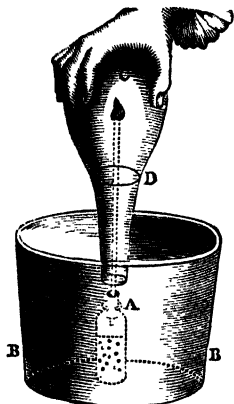


FIG. 22.—Scheele's experiment on the combustion of inflammable air.

Scheele thought that hydrogen (inflammable air) was phlogiston, and in considering the last experiment he asked himself :

- (1) What has become of the fire air ?
- (2) Where has the phlogiston (inflammable air) gone ?

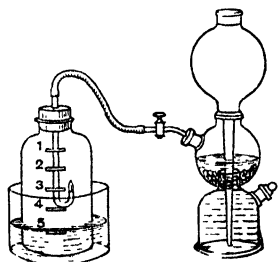


FIG. 23.—Combustion of hydrogen in air.

The fire air, he argued, must either remain in the air, be dissolved in the water, or have escaped through the vessel. He did not notice the *moisture* (which contained both the missing gases) condensed on the flask because he worked over hot water, which gave off steam. The foul air was lighter than common air, although the air had undergone a contraction, hence the two substances cannot be present in it, and he found nothing in the water. Scheele concluded that the fire air and phlogiston had escaped through the

glass, combined in the form of fire (heat and light), considered to be material : $\text{fire} = \text{fire air} + \phi$.

Scheele now tried to reverse this change, *i.e.*, to decompose heat into fire air and phlogiston. For this purpose he must present to the heat a substance having a greater attraction for phlogiston than is shown by fire air, when the latter should be set free. He chose *nitric acid* because it readily corrodes metals, taking out their phlogiston and forming red fumes. In order to subject it to the action of heat, the acid must be

fixed, and Scheele did this by combining it with potash, and setting the acid free at a high temperature by distilling the nitre with strong oil of vitriol (sulphuric acid) in a retort (Fig. 24). Red fumes came off,

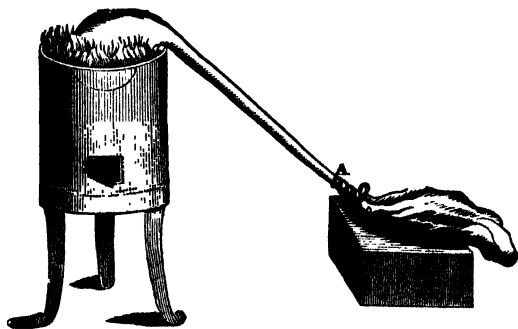
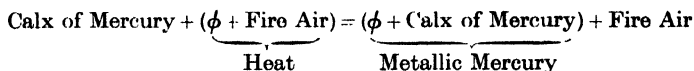


FIG. 24.—Scheele's isolation of fire air.

which were absorbed in a bladder containing milk of lime attached to the neck of the retort. The bladder gradually filled with a colourless gas in which a taper burned with a flame of dazzling brilliance. This was fire air.

Scheele prepared fire air in other ways. He heated calx of mercury (*mercurius calcinatus per se*), which he supposed absorbed phlogiston from the heat, setting free the fire air :



He also obtained fire air by heating "black manganese" (manganese dioxide) with sulphuric or arsenic acid, nitre, magnesium and mercurous nitrates, and silver or mercurous carbonates, the *aerial acid* (carbon dioxide) simultaneously produced from the carbonates being absorbed by means of an alkali : silver carbonate = silver + fire air + aerial acid.

Scheele found that fire air is *completely* absorbed by moist liver of sulphur. When he burnt phosphorus in a thin flask of it, the flask burst on cooling. With a thicker flask, the cork could not be taken out under water but could be pushed in, when water rushed in and filled the flask. A hydrogen flame continued to burn in the gas until seven-eighths were absorbed. When fire air was added to the foul air left after combustion of hydrogen, etc., in air, so as to restore the original volume, the mixture had all the properties of ordinary air, *e.g.* it left the same residue after standing over liver of sulphur.

Fill a gas-jar, divided into 5 parts, four-fifths with nitrogen, and then fill up the remaining fifth with oxygen. Test the gases separately in tubes with a taper, and then the mixture.

Scheele confined animals and insects in air, taking care to put along with them their appropriate foods. He found that they ultimately

died; *aerial acid* (Black's *fixed air*) was produced and a contraction of the air resulted, the residue extinguishing a flame. Similar results were found with sprouting peas. Two large bees were placed in a bottle of fire air over milk of lime, Scheele having "provided some honey for their stay." After eight days the bottle was almost completely filled with liquid, and the bees were dead. He also noticed that fire air is partly dissolved out of common air when this stands over water which has been boiled. A candle burns more brightly in the air expelled from water by boiling than in common air.

Priestley's experiments.—Joseph Priestley (1733–1804), having come into possession of a powerful lens or *burning-glass*, tried by its aid to extract "air" from various chemicals given to him by his friend Warltire. Among these was red precipitate, or *mercurius calcinatus per se*, obtained by heating mercury in air, the nature of which had long been a puzzle. The substances were heated by focusing the sun's rays on them in small phials filled with and inverted over mercury.

"Having procured a lens of twelve inches diameter, and twenty inches focal distance, I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious [*i.e. artificially prepared*: cf. Cavendish's *factitious airs*] would yield . . . With this apparatus, after a variety of other experiments, . . . on the 1st August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found that, by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame."

Both Hales (p. 24), and Priestley in 1772, had obtained oxygen by strongly heating nitre, but both had failed to recognise (as Scheele did) that it was a gas different from common air. Priestley did not completely recognise this until March, 1775.

Priestley found that a mouse lived twice as long in the new air as in the same confined volume of common air, and revived afterwards when taken out. He breathed it himself, and fancied his "breast felt peculiarly light and easy for some time afterwards"—hence he recommended its use in medicine (it is now used in the treatment of gas poisoning and pneumonia). "Who can tell but that, in time, this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it." He suggested that by blowing fires with the new air, very high temperatures might be attained, and his friend Mitchill was later on able to melt platinum in this way.

Priestley assumed, from the teachings of Stahl, that a candle on burning gives out phlogiston and is extinguished after a time in a closed vessel because the air becomes saturated with phlogiston. Ordinary air supports combustion because it is only partly saturated with phlogiston and can absorb more of it. Substances burn in air with only a moderate flame, whereas in the new air the flame is vivid; therefore the new gas must contain little or no phlogiston, and hence Priestley

called it *dephlogisticated air*. The gas left when bodies burn out in ordinary air was named, for a similar reason, *phlogisticated air* :

Dephlogisticated Air = Air - ϕ . (Scheele's Fire Air ; Oxygen.)

Phlogisticated Air = Air + ϕ . (Scheele's Foul Air ; Nitrogen.)

Priestley believed that " phlogiston is the same thing as inflammable air [hydrogen], and is contained in a combined state in metals, just as fixed air is contained in chalk and other calcareous substances ; both



LAVOISIER.

being equally capable of being expelled again in the form of air [by the action of acids]."

Owing to his attachment to the phlogiston theory (in which he believed till his death) Priestley was not able to give a correct explanation of his experiments. This was first done by Lavoisier.

Lavoisier's Theory.—Antoine Laurent Lavoisier (1743-1794), the famous French man of science, began to experiment on combustion in 1772. He found that metals when calcined increase in weight, as pointed out by Rey in 1630, and an equal weight of air is absorbed. In a given volume of air calcination proceeds to a fixed limit, and an unabsorbed gas remains. Phosphorus burns in a confined volume of air: the diminished volume extinguishes a taper, and the white powder formed

weighs more than the phosphorus. He concluded that *substances on burning take something from the air*.

Lavoisier modified Boyle's experiment of calcining tin and lead by using weighed *sealed* retorts. He found no change in weight (which disproved Boyle's theory of the fixation of igneous corpuscles) until air was allowed to enter. On heating the calx of lead with charcoal it lost in weight and "an air was abundantly evolved." Thus something is taken from the calx in forming the metal, and this must be "an air."

In October, 1774, Priestley visited Paris with Lord Shelburne, and told Lavoisier at dinner of his discovery of dephlogisticated air, saying he "had gotten it from *precip. per se* and also *red lead*"; whereupon, he says, "all the company, and Mr. and Mrs. Lavoisier as much as any, expressed great surprise." Lavoisier was quick to see the important

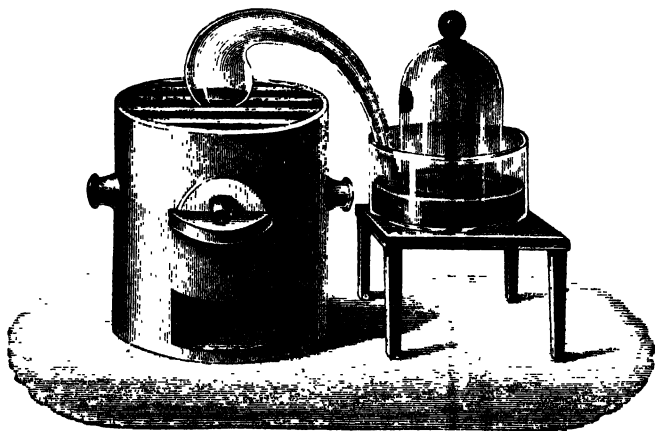


FIG. 25.—Demonstration of the composition of air by Lavoisier (1789).

bearing of Priestley's discovery on his own unfinished work, and he was able to prove that *dephlogisticated air is absorbed in the calcination of metals* by a famous experiment, described in his *Traité de Chimie* (1789).

He heated 4 oz. of mercury in a retort which communicated with a measured volume of air in a bell-jar over mercury (Fig. 25). The volume of air in the bell and in the retort was 50 cu. in. After a time red specks and scales of calx formed on the surface of the mercury. After twelve days the scales no longer increased; the fire was removed, and the experiment stopped. The air had contracted to 42 cu. in., and the gas left was a "mephitic air," which Lavoisier at first called *atmospheric mofette*.* The scales of mercury calx (*mercurius calcinatus per se*) were collected and found to weigh 45 grains. They were transferred to a small retort and heated; 8 cu. in. of dephlogisticated air, which was "an elastic fluid, much more capable of supporting respiration and combustion than ordinary air," and hence called by Lavoisier *vital air* or *air eminently respirable*, were obtained,

* *Mephitis*, a noxious exhalation from the ground, Vergil, *Aeneid*, vii. 84.

together with $41\frac{1}{2}$ grains of mercury. When this vital air was added to the atmospheric mofette, ordinary air was formed without any evolution of heat or light, hence air is probably simply a mixture of these two gases (as had previously been suggested by Scheele).

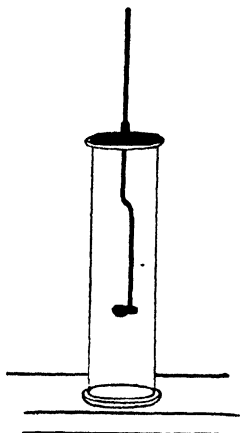


FIG. 26.—Gas jar and deflagrating spoon.

Lavoisier made experiments on the combustion of substances in vital or “pure” air, and summed up his conclusions in four statements which comprise the antiphlogistic theory (1777):

(1) Substances burn only in pure air (oxygen).

(2) Non-metals, such as sulphur, phosphorus, and carbon, produce acids on combustion; hence the gas was called oxygen (from two Greek words meaning “producer of acids”).

(3) Metals produce calces (basic oxides) on absorption of oxygen.

(4) Combustion is in no case due to an escape of phlogiston, but to chemical combination of the combustible substance with oxygen.

Lavoisier’s experiments may be repeated by burning sulphur, phosphorus, and carbon in jars of oxygen, the substances being held by deflagrating spoons (Fig. 26), and shaking the products with litmus solution. The latter is reddened. Magnesium ribbon burns with a blinding light giving a white calx, which turns moist red litmus paper blue.

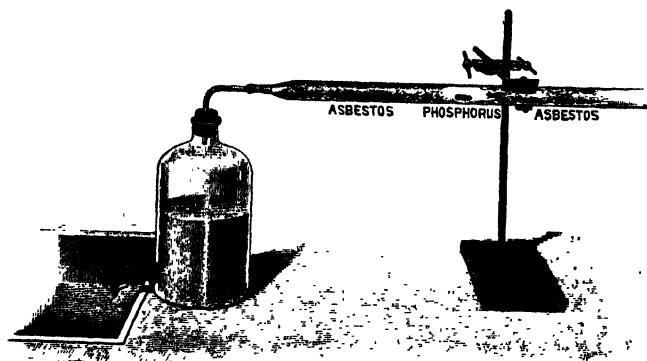


FIG. 27.—The oxidation of phosphorus.

The increase in weight when phosphorus burns may be shown by the following experiment. A small piece of dry phosphorus is placed between two plugs of asbestos in a glass tube (Fig. 27) and the tube weighed. It is attached to an aspirator bottle from which a slow stream of water is allowed to run, thus causing a current of air to pass through the tube. The tube is heated gently until the phosphorus takes fire. The white fumes produced in the combustion are mostly retained by the asbestos. When combustion

ceases, the tube is allowed to cool and weighed. It will have gained in weight.

Lavoisier's new theory was not accepted at once ; Black in England and a few French chemists supported it, but there was a difficulty to be overcome. A metal like zinc dissolves in acid giving inflammable air, and a salt is left on evaporating the solution, which, on strong heating, parts with its acid and leaves the calx of the metal. The same salt is formed when the calx is dissolved in the acid, but no inflammable air is then evolved. Whence comes the inflammable air in the first experiment? This was an easy question for the phlogistonists. The metal contains phlogiston as well as calx, so that in reacting with the acid it evolves this phlogiston as inflammable air. Lavoisier's theory could give no explanation of the origin of the inflammable air ; this was first supplied by the researches of Cavendish on the formation of water from inflammable air and dephlogisticated air.

CHAPTER IV

THE COMPOSITION OF WATER

Cavendish's experiments.—Inflammable air was first collected by Boyle. He filled a bottle with dilute sulphuric acid, put some iron nails in it, and inverted the bottle in a dish of the acid. Bubbles of gas rose from the iron and collected in the bottle. Boyle in 1672 also described the combustibility of hydrogen and showed that a hydrogen flame is extinguished in an exhausted receiver. In 1776 Macquer noticed that a hydrogen flame deposits moisture on a cold saucer. Priestley in 1781 observed that when a mixture of *dephlogisticated air* (oxygen) and *inflammable air* (hydrogen) is kindled it explodes violently. Warltire noticed that when the mixture of gases in a closed glass vessel was kindled by an electric spark, the inside of the vessel, after cooling, was bedewed with moisture.

Collect a mixture of 2 vols. of hydrogen and 1 vol. of oxygen in a strong soda-water bottle over water. The bottle is wrapped in a strong towel, with a short length of neck only projecting, and the whole placed in a strong tin can or iron mortar. Kindle the gas by a long taper. There is a loud explosion.*

By firing the gases in a copper globe with the electric spark Priestley thought he found a slight loss of weight, which he put down to the escape of heat.

Cavendish in 1781 ignited a mixture of common air and inflammable air in a glass globe by means of an electric spark. He found that, with 423 vols. of inflammable air to 1000 vols. of common air, "almost all the inflammable air and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass." There was no change in weight after explosion.

To examine the nature of the dew, Cavendish performed an experiment similar to the following.

Burn a jet of hydrogen, dried by calcium chloride, under a glass flask cooled by running cold water (Fig. 28). Notice the collection of moisture on the outside of the flask, which drops off and may be collected in a small dish. It will be found that this liquid is odourless, tasteless, boils at 100°, and leaves no residue on evaporation. It is water.

Cavendish prepared a mixture of 195 vols. of dephlogisticated air (oxygen) and 370 vols. of inflammable air (hydrogen) in a bell jar over water. The end of a siphon tube, attached to the previously exhausted

* This and similar experiments must be performed with adequate precautions to prevent injury in case the bottle should burst.

glass firing-globe or *eudiometer* (Fig. 29), was covered with a bit of wax and passed inside the jar. The wax was knocked off and on opening

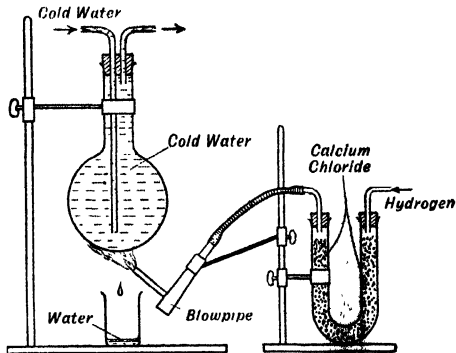


FIG. 28.—Formation of water by the combustion of hydrogen in air.

the stopcock the globe was filled with the gas mixture. The tap was closed and the mixture fired by a spark. The gas "lost its elasticity," and on opening the stopcock the globe was again filled with the gas, which took the place of that converted into liquid water by the explosion. This was repeated six times, and water was produced. The ratio of the combining volumes of hydrogen and oxygen found in these experiments was 201 : 100.

Cavendish found that the water produced in this experiment was acid. He proved that the acidity was due to nitric acid, formed only with oxygen in excess and due to the combination with oxygen of nitrogen present in it as an impurity. Acid is not produced in explosion of hydrogen with *air*, because the flame is then not hot enough.

Cavendish's experiments on the cause of the acidity of the water delayed publication of his memoir until 1784. His conclusions were: "I think we must allow that dephlogisticated air is in reality nothing but dephlogisticated water; and that inflammable air is either pure phlogiston, as Dr. Priestley and Mr. Kirwan suppose, or else water united to phlogiston," and in all probability the latter. This would represent the formation of water as follows :

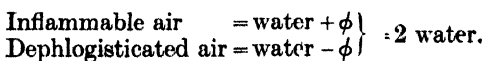


FIG. 29.—Cavendish's firing globe ("Eudiometer").
(From a photograph of what is believed to be the original apparatus in the University of Manchester.)

Cavendish took (water + ϕ) for inflammable air, because a red heat is necessary to start the combination of the two gases, whereas nitric oxide (*cf.* p. 26) combines with dephlogisticated air (oxygen) at the ordinary temperature, and in presence of water forms nitric acid. Nitric oxide is produced by the action of copper on nitric acid, and was regarded as (nitric acid + ϕ). It is improbable that dephlogisticated air should be able to separate ϕ from its combination with nitric acid but not able to unite with



CAVENDISH.

free ϕ (if this is inflammable air) under the same conditions. Hence inflammable air is probably not pure phlogiston, but phlogisticated water. Cavendish therefore thought that water pre-existed in the two gases, and its formation on explosion was simply due to a transfer of phlogiston. James Watt is sometimes credited with stating, in a letter published in 1784, that water is *composed* of the two gases, but there are reasons for doubting this.

Lavoisier's explanation of Cavendish's experiments.—Lavoisier had been puzzled by the combustion of hydrogen in oxygen, which he thought should produce an acid. In 1783 he resolved to make the experiment of burning hydrogen in oxygen on a larger scale, so that the product, whatever it was, should not escape his notice. In May or June

of that year Sir Charles Blagden, formerly Cavendish's assistant, visited Lavoisier and told him of Cavendish's experiments. Lavoisier saw the importance of the result, and on 24th June, 1783, he repeated the experiments in the presence of Blagden. On the following day an account of them was sent to the French Academy of Sciences, and was published in the *Mémoires* in 1784. Practically no mention is made of Cavendish, whose paper did not appear until 1784. Lavoisier has no claim to the discovery of the composition of water, but he must be given the credit of having first clearly stated the results. "Water is nothing but oxygenated hydrogen or the immediate product of the combustion of oxygen gas with hydrogen gas, deprived of the light and caloric (heat) which disengage during the combustion."

In 1784 Lavoisier and Meusnier decomposed water by passing steam over iron borings heated to redness in a gun-barrel. Hydrogen was liberated and the iron converted into the same black oxide as is produced when iron wire burns in oxygen.

A piece of *weldless* iron pipe loosely packed with small iron nails is connected with a flask of water at one end, an empty flask and gas delivery tube being at the other, as shown in Fig. 30. Heat the iron pipe to redness and boil the water in the flask. Water collects in the empty flask, showing that the decomposition is not complete, but bubbles of gas are evolved from the delivery tube. Show that this is hydrogen. After the experiment examine the residue in the tube.

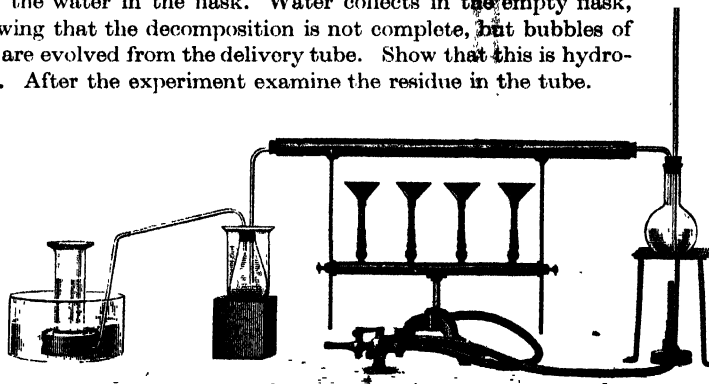


FIG. 30.—Decomposition of steam by red-hot iron.

Insert a piece of burning magnesium ribbon into a large conical flask in which water is boiling vigorously. The metal burns brightly in the steam, the hydrogen produced burns when kindled at the mouth of the flask, and white magnesium oxide remains.

Lavoisier was now able to explain the difficulty mentioned on p. 35, and so remove the last argument in favour of the phlogiston theory. A metal such as zinc, when dissolving in dilute acid, decomposes the water, liberating hydrogen and combining with oxygen of the water to form the calx (oxide), which then unites with the acid to form a salt. The origin of the inflammable gas was therefore cleared up. Lavoisier regarded the acid as an oxide; at the present time the hydrogen is regarded as coming from the acid.

From 1785 the theory of phlogiston soon disappeared and modern chemistry had its origin in Lavoisier's writings. The material had been collected by the investigations of Boyle, Priestley, Cavendish, and Scheele, but it required the clear and original mind of the great French chemist to explain it and to form it into a logical system.

Monge in 1783 exploded hydrogen and oxygen, drawn from two graduated jars into a previously evacuated glass globe with firing wires (Fig. 31). No fewer than 372 successive explosions were made,

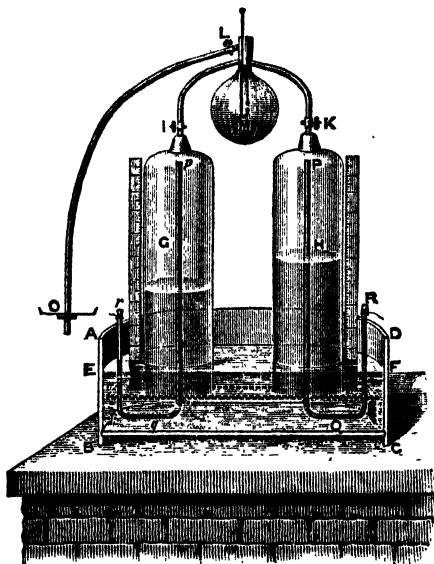


FIG. 31.—Monge's experiment of the combination of hydrogen and oxygen gases.

The gases were collected through siphon tubes, *pr*, *PB*, in the graduated cylinders, *G* and *H*; they passed through the stopcocks, *I* and *K*, to the globe, *M*, previously exhausted through the tap, *L*, leading to an air-pump at *O*.

producing four ounces of water, and the hydrogen and oxygen combined in the ratio of 1.95 : 1 by volume. The result is less accurate than Cavendish's.

The electrolysis of water.—In 1800 Nicholson and Carlisle, and Cruickshank, experimenting with the newly-invented electric battery of Volta, discovered that bubbles of oxygen and hydrogen, respectively, rise from two platinum wires connected with the copper and zinc poles of the battery and dipped into water. From copper or iron wires hydrogen only comes off; the oxygen is absorbed by the wire, producing an oxide. They collected the gases separately and found that 2 vols. of hydrogen and 1 vol. of oxygen are liberated. This agrees with Cavendish's synthesis of water. Davy in 1806 showed that when very pure water is electrolysed in a gold vessel, and the experiment is carried out in a vacuum receiver so that no impurities can enter from the air, or

be dissolved from glass or other substances of ordinary vessels, then nothing but hydrogen and oxygen are produced. *Water is decomposed by an electric current into hydrogen and oxygen in the ratio of 2 to 1 by volume.*

An apparatus for the decomposition or **electrolysis** of water by an electric current is shown in Fig. 32. It is called a **voltmeter** or **coulometer** and consists of two glass tubes with stopcocks above, connected by a horizontal tube, carrying a funnel for filling the apparatus with water to which a little sulphuric acid, has been added to render it a conductor of electricity. Pure water is a bad conductor, but only the water is decomposed in the process. The **electrodes** leading the current into and out of the liquid consist of platinum foil. The current may conveniently be taken from accumulators in series.

Bubbles of gas rise from each electrode; that coming from the positive electrode, although it appears more abundant because it is liberated in smaller bubbles (according to Faraday because the platinum is cleaner), occupies half the volume of the other gas, and if allowed to escape from the tap inflames a glowing chip of wood. This gas is oxygen. The gas evolved from the negative electrode, when kindled by a taper, burns with a flame, and is hydrogen.

Electrolytic gas.—Two electrodes are placed in a bottle of dilute acid (Fig. 33): the hydrogen and oxygen gases come off mixed together in the form of **electrolytic** or **detonating gas**. This is washed free from acid spray by

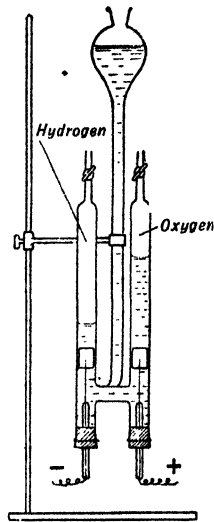


FIG. 32.—Decomposition of water into hydrogen and oxygen by electrolysis.

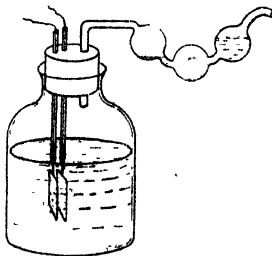


FIG. 33.—Preparation of electrolytic gas.

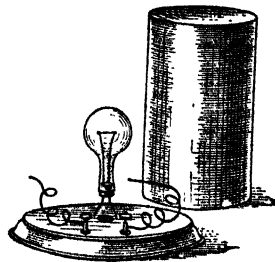


FIG. 34.—Explosion of electrolytic gas by an electric spark.

water in the bulb tube, and collected over water in a small *thin* glass flask. This when filled with the mixture is inverted over a cork carrying two copper wires connected with a coil (Fig. 34). The flask is covered with a cage of stout fine-mesh iron wire gauze and a spark passed. There is a violent detonation and the flask is shattered, a little fine powder escaping through the gauze in the form of smoke.

The composition of water by volume.—The composition of water by volume may be found fairly accurately by the following experiment (see p. 188 for a very accurate method).

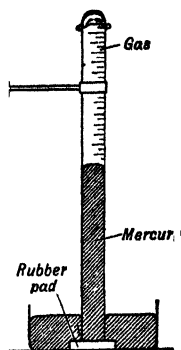


FIG. 35.—Bunsen's eudiometer, for exploding a mixture of gases confined over mercury.

Bunsen's eudiometer (Fig. 35) * consists of a strong glass tube sealed at one end and provided with two platinum wires sealed through the glass for the purpose of passing an electric spark. It is graduated almost to the open end in mm. which are taken as measuring the volumes, since except at the closed end the cross-section is constant.

The eudiometer is filled with mercury and inverted over mercury in a trough. Pure hydrogen is passed in and the volume accurately read off, the corrections for temperature and pressure (see Chapter V) being applied, the distance of the mercury meniscus in the tube from the level in the trough being subtracted from the barometer reading. A volume of pure oxygen rather less than a quarter that of the hydrogen is then added.†

The open end of the eudiometer is held down firmly on a pad of rubber beneath the mercury and an electric spark from a coil is passed. There is a flash of light in the tube and a dull noise is heard. Dew appears on the walls of the tube after cooling.

The eudiometer after cooling is lifted from the rubber pad and the volume of moist hydrogen remaining is read off and corrected for temperature and pressure. It will be found that the two gases have combined in the ratio of 2 volumes of hydrogen to 1 volume of oxygen. That the residual gas is hydrogen may be confirmed by testing it with a taper.

The volume composition of steam.—In order to find the volume of steam produced from the combination of the gases, if it were kept gaseous, it is convenient to use a U-shaped eudiometer, the closed limb of which is surrounded by a glass jacket through which the vapour of boiling amyl alcohol (132°) is passed. The water produced is then kept in the form of vapour (Fig. 36).

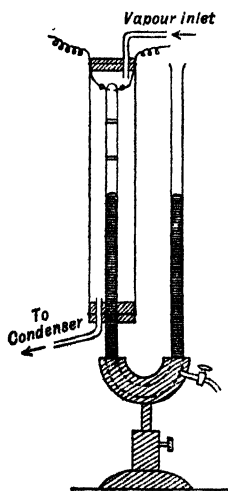


FIG. 36.—Volume composition of steam.

Twenty ml. of hydrogen and 10 ml. of oxygen are introduced, measured at the temperature of the jacket with the mercury levels adjusted to equality on both sides. The open end of the U-tube is firmly closed by a rubber stopper, and a spark passed from the coil. There is a flash of light and an

* A more convenient but more complicated and expensive apparatus is described in Chapter XXIX.

† The explosion is less violent than with a 2 : 1 mixture.

immediate contraction. By taking out the stopper and running mercury into the open limb until the levels are again equal, it will be seen that the steam occupies 20 ml. :

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of steam.

If the *densities* of oxygen and hydrogen gases are known the experiment will enable us to calculate the composition of water by weight.

The density of oxygen at S.T.P. is 1.429 gm. per litre, that of hydrogen is 0.09 gm. per litre. The weight of two litres of hydrogen is 0.18 gm., and this combines with 1 litre, or 1.429 gm., of oxygen. Hence the weight of oxygen combining with 1 gm. of hydrogen is $1.429/0.18 = 7.94$ gm.

More accurate experiments on the combining volumes of hydrogen and oxygen are described in Chapter XIII.

The composition of water by weight.—Since it is difficult to weigh with accuracy large volumes of hydrogen and oxygen, the composition of water by direct synthesis from its elements was attempted only comparatively recently. Formerly an indirect method was used. A stream of dry hydrogen, which is not weighed, is passed through a weighed tube containing copper oxide (prepared by heating copper turnings in air) heated to dull redness. The oxide is *reduced* by the hydrogen to metallic copper, the oxygen of the copper oxide uniting with the hydrogen to form water, which is collected in a weighed calcium chloride tube and weighed.

About 20 gm. of black oxide of copper, previously heated to redness in a crucible and cooled in a desiccator over calcium chloride to remove moisture, is introduced into a hard glass tube (Fig. 37), which is then weighed. The

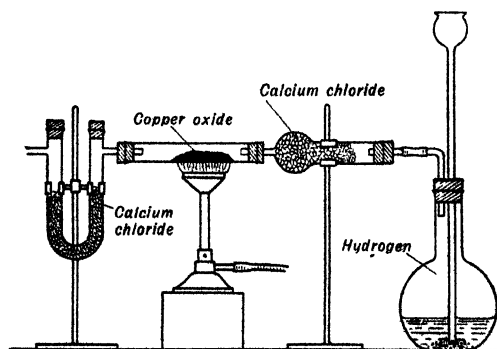


FIG. 37.—Composition of water by weight.

tube is connected by a rubber stopper to a large weighed U-tube containing granular calcium chloride, which readily absorbs water vapour.

A current of hydrogen generated from pure zinc and dilute sulphuric acid in the flask, and dried by a calcium chloride tube, is passed through the apparatus until all the air is expelled. The copper oxide is then heated.

Drops of moisture condense in the tube, and the black oxide of copper is reduced to red metallic copper. As the experiment proceeds and the tube becomes warm, all the water is driven over into the calcium chloride tube. The apparatus is allowed to cool, with hydrogen still passing. The tube containing the copper and the U-tube are again weighed.

From these results we find :

Loss of weight of copper oxide
= weight of oxygen = o .

Weight of water - weight of oxygen
= weight of hydrogen = h .

\therefore ratio of combining weights = o/h .

It will be seen that the weight of hydrogen is obtained by difference, so that the synthesis is not complete. This method was used by Berzelius and Dulong in 1819, who found the ratio oxygen : hydrogen = 8.01 : 1.

Dumas' experiment.—In 1842 Dumas carried out this experiment with greater accuracy. Hydrogen generated from zinc and dilute sulphuric acid was purified by passing through seven U-tubes containing : (1) lead nitrate solution to remove hydrogen sulphide, (2) silver sulphate solution to remove arsenic hydride, (3) three tubes of potassium hydroxide to remove acid vapours, (4) two tubes of sulphuric acid cooled in ice, or else phosphorus pentoxide, to dry the gas. The reagents were spread on pumice or broken glass to expose a large surface. These were followed by a *témoin* (or "witness") tube, the weight of which must remain unchanged when the drying has been as effective as possible : it contained sulphuric acid or phosphorus pentoxide.

The copper oxide was contained in a large hard-glass bulb with a long neck, weighed after evacuation to remove air. The air was displaced from the apparatus by hydrogen, and the bulb heated by a large spirit lamp for ten to twelve hours. The water produced was collected in a smaller bulb, in the neck of which calcium chloride was placed, followed by a series of four drying tubes containing sulphuric acid on pumice, or phosphorus pentoxide. The last tube communicated with a vessel of sulphuric acid, through which the residual hydrogen escaped. In all the experiments the weight of the last absorption tube was constant. The whole apparatus is shown in Fig. 38.

The copper was allowed to cool in the bulb in a stream of hydrogen, the hydrogen was displaced by air in the whole apparatus, and the bulb then exhausted and weighed. The absorption system was also weighed.

A mean of nineteen experiments gave the following result :

	Percentage by weight.	Combining ratio by weight.
Oxygen	88.864	7.98
Hydrogen	11.136	1.00
	<u>100.000</u>	<u>8.98</u>

This ratio was accepted without question for nearly half a century. Dumas himself, however, had pointed out two sources of error in the method :

(1) Air dissolved in the sulphuric acid passed on with the hydrogen,

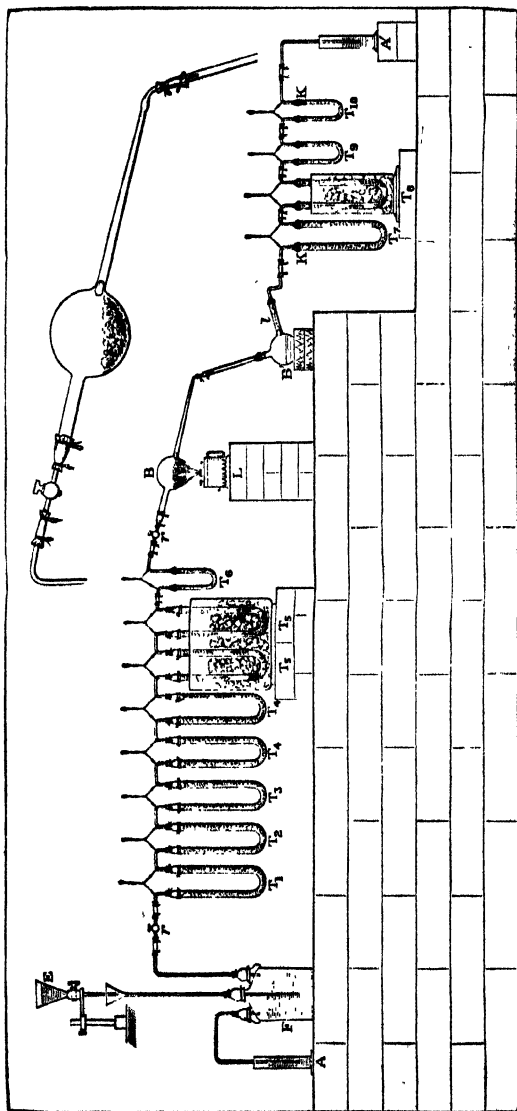


FIG. 38.—DUMAS' APPARATUS FOR DETERMINING THE COMPOSITION OF WATER.

The copper oxide bulb, B, is shown above on a larger scale. The apparatus consisted of the following parts: F, a Woulfe's bottle for the generation of hydrogen; E, a tap-funnel containing sulphuric acid; A, a mercury safety-valve; T₁, a tube containing lead nitrate solution spread on broken glass; T₂, a tube containing glass moistened with silver sulphate solution; T₃, a tube containing (a) pumice soaked in potash solution, (b) solid potash; T₄, tubes containing pieces of potash; T₅, T₆, tubes containing phosphorus pentoxide (or sometimes sulphuric acid spread over pumice, cooled in a freezing mixture); T₇, a *témoin* tube containing phosphorus pentoxide (or sulphuric acid and pumice); B, the bulb containing copper oxide, with stopcock and pointed tube delivering into the receiver, B', for collecting the water, with fragments of calcium chloride at *l*; L, a large spirit lamp for heating the bulb; T₈, a tube of solid phosphorus pentoxide (or sulphuric acid on pumice, cooled in a freezing mixture); T₉, a *témoin* tube of phosphorus pentoxide, or sulphuric acid; T₁₀, a guard-tube of phosphorus pentoxide (not weighed) to exclude moisture; A', escape-valve for excess of hydrogen, containing sulphuric acid.

and the oxygen of this air combined with hydrogen in the copper oxide bulb; (2) the reduced copper retained hydrogen when cooled in that gas.

Both errors tended to reduce the loss of weight of the bulb, so that the proportion of oxygen found should be too small. All later experiments found, however, that the proportion of oxygen given by Dumas was rather too large.

Keiser in 1888 introduced the method of weighing the hydrogen absorbed in metallic palladium; he weighed the water formed on pumping the gas over heated copper oxide, which was not weighed. Oxygen was found by difference.

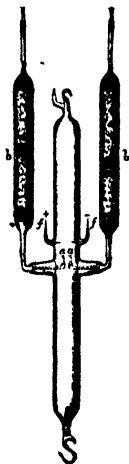


FIG. 39.—Morley's apparatus. The *dry* gases passed through phosphorus pentoxide tubes, *b, b*, to the jets, *a, a*, where they were ignited by electric sparks between wires from the electrodes, *f* and *f*.

Morley's experiments.—Some very accurate experiments on the composition of water by weight were made by the American chemist E. W. Morley from 1880 to 1895. Purified oxygen and hydrogen gases were weighed in large glass globes; in the later experiments the hydrogen was weighed in a bulb containing palladium, which has the unique property of absorbing large volumes of hydrogen but not other gases. When the palladium charged with hydrogen is strongly heated pure hydrogen is evolved. The gases were burnt at platinum jets in a previously evacuated sealed glass vessel (Fig. 39) immersed in cold water. The water collecting in this tube was then frozen, and the residual gas pumped out through a tube containing phosphorus pentoxide (to keep back water vapour) and analysed.

A typical experiment furnished the following data :

Weight of hydrogen introduced into apparatus	=	3.8223 gm.
" residual hydrogen	=	0.0012 "
∴ " hydrogen burnt	=	3.8211 "
" oxygen introduced into apparatus	=	30.3775 "
" residual oxygen	=	0.0346 "
∴ " oxygen burnt	=	30.3429 "
Sum of weights of hydrogen and oxygen burnt	=	34.1640 "
Weight of water produced	=	34.1559 "
∴ Loss in weight due to experimental error	=	0.0081 "

Ratio of weights of oxygen and hydrogen combining to form water = 7.941 : 1.

As a final result, the mean of twelve experiments in which 400 gm. of water were produced, Morley obtained the ratios :

oxygen : hydrogen = 7.9396 : 1
 water : hydrogen = 8.9392 : 1.

In another series of experiments on the densities and combining volumes of the two gases (p. 51), Morley found the ratio :

$$\text{oxygen : hydrogen} = 7.9395 : 1.$$

As is explained later (p. 88) the combining weight of hydrogen is taken as that combining with 8.000 parts by weight of oxygen. Morley's result gives for this $8.000/7.9396 = 1.00673$.

Noyes' experiments.—In 1907 W. A. Noyes improved a method he had used in 1890 for determining the combining weight of hydrogen. In one set of experiments, pure hydrogen was absorbed in palladium in an exhausted tube which was weighed (Fig. 40). Pure oxygen was then admitted and the tube heated, when the hydrogen in the palladium burned to steam which condensed to liquid water in a cooled extension limb of the tube. The tube and water were then weighed and connected with an apparatus in which the water was collected and weighed, the residual gas being pumped off, measured and analysed, and its weight applied in correcting the result. Noyes also used copper oxide in the tube and admitted pure hydrogen to it. The results for copper oxide gave somewhat lower numbers; those for palladium and the purest hydrogen (from electrolysis of baryta solution), which Noyes considered the best, gave the weight of hydrogen combining with 8.000 parts of oxygen as 1.00787. The accepted modern value is 1.0080.

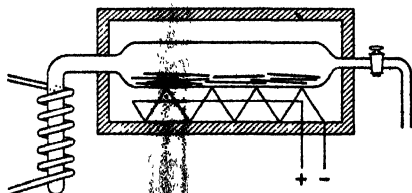


Fig. 40.—Noyes' apparatus.

CHAPTER V

THE PHYSICAL PROPERTIES OF GASES AND VAPOURS

Effect of pressure on the volume of a gas.—Boyle's Law (1662) states that : *at constant temperature the volume of a given mass of gas is inversely proportional to the pressure :*

$$\therefore pV = \text{constant} \dots \dots \dots (1)$$

The density of a gas is the mass per unit volume, m/v , hence *the density is proportional to the pressure.*

Boyle's law is not exact ; all gases show marked deviations from it at high pressures. At moderate pressures all common gases except hydrogen are more compressible than an ideal gas which obeys Boyle's law. Hydrogen is slightly less compressible and the same behaviour is shown by all gases at very high pressures (Amagat). Amagat's results for three gases are shown in Fig. 41, in which $pV = 1$ corresponds with an ideal gas.

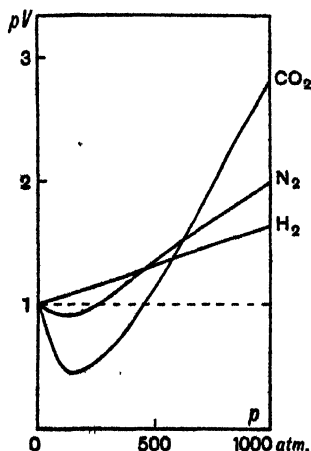


FIG. 41.—Isothermals (50° C.) of gases at high pressures.

It is seen that at all pressures pV for hydrogen is increasingly greater than 1, *i.e.* hydrogen is *less* compressible than an ideal gas (V greater than ideal for all values of p); while nitrogen and carbon dioxide are *more* compressible at moderate pressures, but become less and less compressible at high pressures. Hydrogen was called by Regnault *plus que parfait*, but all gases behave like it at high pressures.

At very low pressures (0.01 – 1.5 mm. Hg) no deviation from Boyle's law can be detected (Rayleigh, 1901-2), and the gases behave as ideal (see p. 105).

Effect of temperature on the volume of a gas.—Dalton in 1801 observed that gases expand by equal increments of volume for equal rises of temperature; his results were published in 1802. In 1802 Gay-Lussac published a memoir in which he stated that Charles in 1787 had found that gases expand equally between 0° and 80°, but did not measure the expansion. Gay-Lussac from his own experiments derived the law in question, which differs from Dalton's in the reduction of the initial volume to 0°. It is usually known as **Charles's law**: *at constant pressure all gases expand by 1/273 of their volume at 0° C. for a rise in temperature of 1° C.*

Let v_0 = volume at 0° , v_t = volume at t° , under the same pressure, then $v_t = v_0(1 + t/273)$, or $v_t/v_0 = (273 + t)/273$. If v_1, v_2 are the volumes corresponding to two temperatures t_1°, t_2° , then:

$$v_2/v_1 = (273 + t_2)/(273 + t_1).$$

The value $(t + 273)$ is the absolute temperature, T , corresponding to t ; hence, the volumes of a given mass of gas at constant pressure are proportional to the absolute temperatures: $v_2/v_1 = T_2/T_1$. If $t_2 = -273^\circ \text{C.}$, then $T_2 = 0$, and by substitution in the equation we find $v_2 = 0$. Before this temperature is reached on cooling, however, all gases are liquefied. The temperature -273°C. is the zero of absolute temperature, or the absolute zero.

If the volume of a given mass of gas is kept constant, the pressure increase for 1° is $1/273$ of the pressure at 0° . This is readily proved from Boyle's and Charles's laws. Thus $p_2/p_1 = T_2/T_1$.

If volume and temperature of a given mass of gas change together, the equation $p_1v_1/T_1 = p_2v_2/T_2$ or, generally, $pv/T = \text{constant}$, can be deduced as follows:

Change from the initial state (p_1, v_1, T_1) to the final state (p_2, v_2, T_2) in two steps:

(i) p_1 to p_2 keeping T_1 constant. Let v_1 become V . By Boyle's law: $V = p_1v_1/p_2$.

(ii) T_1 to T_2 keeping p_2 constant. V changes to v_2 . By Charles's law: $v_2/T_2 = V/T_1$. Eliminate V $\therefore p_1v_1/T_1 = p_2v_2/T_2$.

Charles's law is not strictly true; the coefficients of expansion of different gases are not quite equal, and differ slightly from $1/273$, and the change of pressure at constant volume is slightly different from the change of volume at constant pressure, for the same rise of temperature. At very low pressures, however, the coefficients approach the limiting value $1/273.09$. For the ideal gas the coefficient of expansion is $1/273.09 = 0.0036618$.

The density of a gas.—The density of a gas or vapour is expressed in two ways:

(1) The normal density (or simply density) of a gas is the weight in grams of 1 litre measured at a temperature of 0°C. , and under a pressure of 760 mm. of mercury at 0°C. , at sea-level and latitude 45° .

The weight of the mercury column in the barometer, and hence the pressure, varies slightly with the variation of the acceleration of gravity g at different heights above sea-level and at different latitudes, hence in accurate work the standard conditions of sea-level and latitude 45° are specified.

(2) The relative density of a gas or vapour is the weight of any volume of it divided by the weight of an equal volume of pure hydrogen, under the same conditions. Hydrogen is chosen as the standard substance because it is the lightest gas known.

Relative densities so defined are not used in accurate work, since different gases and vapours behave somewhat differently towards temperature and pressure changes.

Standard temperature and pressure (or normal temperature and pressure), denoted by S.T.P. (or N.T.P.), are 0°C . (273.09° absolute), and the pressure of a column of 760 mm. of mercury at 0°C . at sea-level, and at latitude 45° . On account of slight deviations of gases from Boyle's and Charles's laws the density in accurate work is determined with the gas actually at S.T.P., so that no corrections by the gas laws are necessary. With vapours an approximate value of the relative density is usually all that is required.

Determination of gas densities.—The density of a gas is determined by weighing an exhausted globe, filling it with the gas, and reweighing. The volume of the globe is determined by weighing it filled with water (see p. 58).

The true weight (in vacuum) of the globe is the apparent weight in air *plus* the weight of air displaced by the globe. The weight of air displaced depends on the temperature, pressure, and degree of moisture of the air, and as these may be different in separate weighings, corrections of all weights to vacuum is necessary in accurate work. Also, the surface of the globe carries a film of moisture condensed upon it from the atmosphere (*cf.* p. 13), which will vary with the moistness of the air. To eliminate these difficulties so far as possible, Regnault in 1845 made

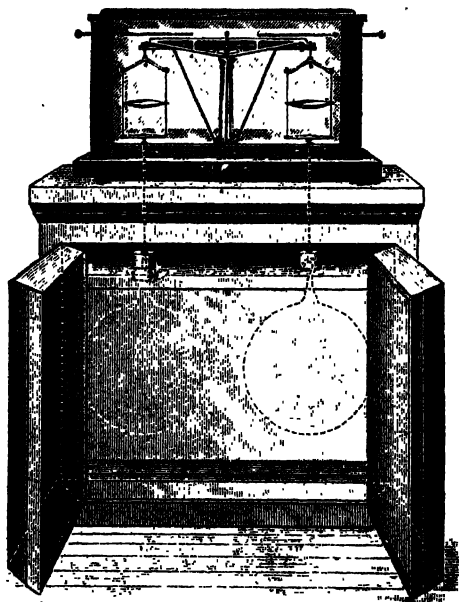


FIG. 42.—Determination of the density of a gas.

use of a compensating globe. The density globe was counterpoised on the balance by hanging on the other arm a second globe of as nearly as possible identical weight and volume (Fig. 42), so that all variations of

atmospheric conditions affect both globes equally, and corrections are eliminated. The small adjustments of weight necessary, corresponding with the weights of the gases themselves, are made with ordinary metal weights, which are corrected to vacuum in calibration and in any case have a negligible displacement.

A correction required in this method pointed out by Lord Rayleigh (1882) is that due to the *shrinkage* of the globe on evacuation. The globe displaces a little less air when it is vacuous than when it is full of gas, or than the compensating globe. The shrinkage is found by pumping out the globe in a closed vessel filled with water, and observing the fall of level of the water in a communicating graduated tube. With a globe of 2 litres capacity the correction to be applied was 0.0006 gm. on the weight of hydrogen filling the globe, and Regnault's value of 0.08965 for the normal density of hydrogen was raised to 0.08988.

This method was used by Morley (1896) in a determination of the normal densities of hydrogen and oxygen. Very pure hydrogen gas was absorbed in metallic palladium contained in a glass tube. This metal, when heated and then cooled in the gas, takes up about 600 times its volume of hydrogen, but not gaseous impurities, so that these are removed by pumping. On heating the palladium charged with hydrogen to dull redness, pure hydrogen is evolved, and the loss in weight of the tube gives the weight of gas. The hydrogen was received in three large exhausted glass globes immersed in ice, the total volume of the globes being accurately known. The rise in pressure in the globes was determined by a mercury manometer. One result is given below.

Volume of the three globes - - - -	43.2574 litres
" " gas space in manometer - -	0.0550 litre
" " connecting tubes - - - -	0.0365 "
	43.3489
Total volume of gas - - - -	43.3489 litres.

Temperature 0°. Pressure 725.40 mm. Hg. Loss of weight of palladium bulb = weight of hydrogen = 3.7164 gm.

Correction to sea-level and latitude 45°, and length of cathetometer to 0° = 1.00044 ;

∴ normal density of hydrogen

$$= \frac{3.7164}{43.3489} \times \frac{760}{725.4} \times 1.00044 = 0.089861 \text{ gm./litre.}$$

As a mean result, Morley found :

normal density of hydrogen = 0.089873 ± 0.000027 gm. per litre
 normal density of oxygen = 1.42900 ± 0.000034 gm. per litre.

In comparing the first figure with the corrected result of Regnault, Morley's must be reduced to the latitude of Paris. His value then becomes 0.089901, differing from Regnault's, 0.08988, by less than 1 in 4000.

The following table gives the exact values of the normal densities of some gases :

Hydrogen	-	-	0.08987	Nitric oxide	-	-	1.3402
Helium	-	-	0.1785	Oxygen	-	-	1.42900
Methane	-	-	0.7168	Hydrogen chloride	-	-	1.6392
Ammonia	-	-	0.7708	Argon	-	-	1.7836
Neon	-	-	0.8999	Carbon dioxide	-	-	1.9768
Carbon monoxide	-	-	1.2504	Nitrous oxide	-	-	1.9777
Nitrogen	-	-	1.2507	Sulphur dioxide	-	-	2.9267
Air	-	-	1.2927	Chlorine	-	-	3.214

The relative density of air is $1.2927 \div 0.08987 = 14.38$. Densities of gases were previously referred to air = 1 instead of to hydrogen = 1; these values may be converted by multiplication by 14.38. The composition, and therefore density, of air vary slightly in different localities, hence this gas is no longer used as a standard of relative density.

The law of partial pressures.—Dalton in 1801 found that when two or more gases which do not react chemically are mixed in a vessel, *the pressure exerted by the mixture of gases is the sum of the pressures which each gas alone would exert if separately confined in the whole volume occupied by the mixture.* (The temperature is assumed to be constant). The pressures exerted by the separate gases are called their **partial pressures**, and the above statement that *the total pressure is the sum of the partial pressures* is called the **law of partial pressures**.

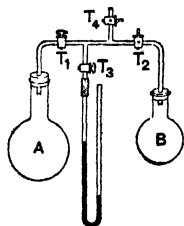


Fig. 43.—Experiment on partial pressures.

Connect two globes, *A* and *B* (Fig. 43), of about 2 and $\frac{1}{2}$ litres, with each other and a manometer as shown. *A* contains air and *B* carbon dioxide. Close the stopcocks T_2 and T_3 and partly evacuate *A* through the cock T_4 . Close T_4 and establish connection with the manometer by opening T_3 . Read the difference in mercury levels, and subtract from the reading of the barometer to find the pressure of the air. Let the pressure in *A* be p_A mm., and the pressure in *B*, p_B mm. Close T_3 and open T_1 and T_2 . When the two gases have mixed open T_3 and read the final pressure, p . Total volume = $v_A + v_B$; \therefore partial pressures of the gases in *A* and *B* respectively are $p_A \cdot \frac{v_A}{v_A + v_B}$ and $p_B \cdot \frac{v_B}{v_A + v_B}$, these, by Boyle's law, being the pressures the separate quantities of gas would exert if each occupied the whole volume $v_A + v_B$. The sum of the partial pressures is $\frac{p_A v_A + p_B v_B}{v_A + v_B}$, and this will be found to be very nearly equal to p .

The law of partial pressures is not strictly exact; all real gases show slight deviations from it. Leduc found that the following law is more exact: *the volume occupied by a mixture of gases is equal to the sum of the volumes which the separate gases would occupy at the same temperature, and under the same pressure, as the mixture.* This has been verified up to 200 atm. pressure.

Vapour pressure.—Liquids admitted to vacuous spaces evaporate or give off vapour, and when excess of liquid is present the vapour reaches a definite pressure, which depends only on the temperature. The vapour is then said to be saturated. Dalton's law of partial pressures shows that the vapour pressure of a liquid in a closed vessel filled with an indifferent gas will be the same as if the space were initially vacuous. If there is not enough liquid present to saturate the space, the vapour is unsaturated and the pressure depends on the volume.

Fill two tubes about 78 cm. long, sealed at one end and carefully cleaned and dried, with dry mercury, and invert in two small dishes containing mercury. The level of the mercury sinks in each tube, leaving a vacuous space above. Measure the level of mercury in each tube above the surface in the dish.

By means of small bent pipettes introduce a few drops of water into one tube, and a few drops of ether into the other. Notice that the depression of the mercury due to the ether is much greater than that caused by the water. Measure the levels and find the vapour pressures at atmospheric temperature. Warm the tube containing ether with the hand and notice the further fall of mercury, due to the increase of vapour pressure with temperature.

The vapour pressure of a liquid increases with the temperature. This is seen from Fig. 44, which is the vapour pressure curve of water. When the vapour pressure becomes equal to the *total* pressure exerted on the surface of the liquid, say by the atmosphere, the liquid boils, *i.e.* vapour is emitted in bubbles throughout the whole bulk of the liquid. The boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure, or other total pressure, acting on the surface. Boiling points are usually given for a pressure of 760 mm., or 1 standard atmosphere.

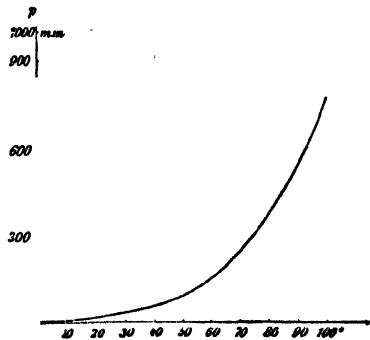


FIG. 44.—Vapour pressure curve of water.

If the pressure on the surface is reduced, say by connecting a flask containing the liquid with a pump, the boiling point is lowered. At a pressure of 17.5 mm., water boils at 20°. It is necessary to specify the pressure in giving a boiling point; unless this is done 760 mm. is understood. The above result would be expressed as: 20°/17.5 mm.

The effect of pressure on the boiling point may be shown by boiling water in a strong *round-bottomed* flask, corking the flask, and pouring cold water over it. Owing to the condensation of steam in the upper part of the flask the pressure is reduced, and the water boils vigorously.

Place a thin glass bulb, containing 2 ml. of bromine (Fig. 45) inside a 500 ml. bottle. Fit to the bottle a rubber stopper, through which pass a glass tube, closed at one end, and with the other end over the point of the bulb below, and a small manometer, containing mercury. Depress the tube so as to fracture the bulb, and observe the rise of pressure indicated by the manometer. Notice the formation of a layer of red bromine vapour in the lower part of the bottle. This diffuses upwards and the pressure rises as the space becomes saturated.

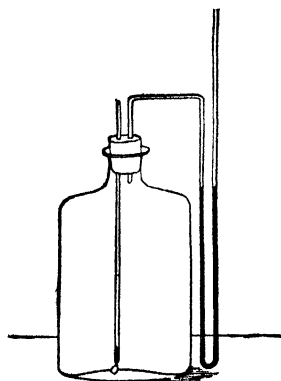


FIG. 45.—Vapour pressure of a liquid in a space filled with gas.

Solids also have definite vapour pressures at different temperatures. These are usually smaller than those of liquids, although solids may, at a given temperature, have greater vapour pressures than liquids of different composition. The vaporisation of solids without previous fusion is called sublimation, although this name is generally used for the vaporisation of a solid and its condensation on a cooler part of the apparatus.

Pass a small piece of camphor into the vacuous space in a barometer tube surrounded above by a hot-water jacket, and notice the fall of the mercury.

Equilibrium.—At a given temperature, liquid (or solid) and vapour can exist indefinitely in contact when the vapour pressure is the maximum at that temperature, *i.e.* when the vapour is saturated. The system composed of two phases, liquid and vapour, is then said to be in equilibrium. An equilibrium state is one which is independent of time. If we represent transition from liquid to vapour by the symbol: [Liquid] \rightarrow [Vapour], *i.e.* evaporation, and transition from vapour to liquid by: [Vapour] \rightarrow [Liquid], *i.e.* condensation, the state of equilibrium will be represented by [Liquid] \rightleftharpoons [Vapour].

The equilibrium between two phases of a *pure substance* exists at a definite pressure, which is independent of the amounts of the two phases and depends only on the temperature.

Moist gases.—In the laboratory, gases are often collected over water, and in accurate measurements it is necessary to correct the volume of the gas for the water vapour in it. When water evaporates into a dry gas at constant pressure the gas will expand. The volume of a given mass of gas is therefore greater when it is moist than when it is dry.

Suppose we have a volume of 100 ml. of moist air, measured over water at 15°, and under a total pressure of 760 mm. This total pressure is, by the law of partial pressures, the sum of the pressure of the dry air and of the vapour pressure of water at 15°, *viz.*, 12.8 mm. The pressure of the dry air is therefore $760 - 12.8 = 747.2$ mm. If the water vapour were removed by a

drying agent from the 100 ml. of moist air contained in a closed vessel, the pressure would therefore fall to 747.2 mm. If we now increased the pressure of the dry air to 760 mm., the volume would, by Boyle's law, become $100 \times \frac{747.2}{760}$ ml., and at 0° this would be $100 \times \frac{747.2}{760} \times \frac{273}{288} = 93.2$ ml.

If a mass of gas saturated with moisture at t° under a total pressure of P mm. occupies V ml., the volume of dry gas at S.T.P. will be :

$$V \times \frac{P-p}{760} \times \frac{273}{273+t} \text{ ml.},$$

where p is the vapour pressure of water at t° .

In using this formula we require a table of vapour pressures of water at different temperatures.

TABLE OF VAPOUR PRESSURES OF WATER.

$t^\circ \text{C.}$	$p \text{ mm.}$	$t^\circ \text{C.}$	$p \text{ mm.}$	$t^\circ \text{C.}$	$p \text{ mm.}$	$t^\circ \text{C.}$	$p \text{ mm.}$
0	4.579	18	15.477	28	28.349	92	566.99
5	6.543	19	16.477	29	30.043	93	588.60
10	9.209	20	17.535	30	31.824	94	610.90
11	9.844	21	18.650	40	55.324	95	633.90
12	10.518	22	19.827	50	92.511	96	657.62
13	11.231	23	21.068	60	149.38	97	682.07
14	11.987	24	22.377	70	233.7	98	707.27
15	12.788	25	23.756	80	355.1	99	733.24
16	13.634	26	25.209	90	525.76	100	760.00
17	14.530	27	26.739	91	546.05	110	1074.6

Intermediate values in the practically useful ranges 0° - 30° and 90° - 100° may be obtained by logarithmic interpolation.

EXAMPLE.—Find the volume, dry and at S.T.P., of 175 ml. of air measured over water at 18° and 749 mm. atmospheric pressure.

$V = 175$; $P = 749$ mm.; $p = 15.48$ mm. (from table); $t = 18^\circ$.

$$\therefore \text{required volume} = 175 \times \frac{749 - 15.48}{760} \times \frac{273}{273 + 18} = 158.5 \text{ ml.}$$

The law of partial pressures applied to vapours is not exact; the vapour pressure of a liquid in a gas is slightly less than *in vacuo*. It is only at low pressures, i.e. at low temperatures, when the vapour pressures are small, that the application is justified. This is very nearly the case at the ordinary atmospheric temperature.

Density of a moist gas.—Consider 1 litre of moist gas at t° , under a pressure P mm., and let p be the partial pressure of aqueous vapour in the gas. The volume of the dry gas at S.T.P. will be :

$$\frac{P-p}{760} \text{ litres.}$$

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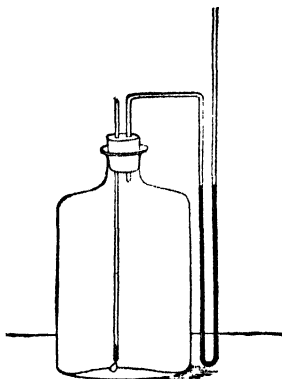


FIG. 45.—Vapour pressure of a liquid in a space filled with gas.

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$$\therefore \text{required volume} = 175 \times \frac{749 - 15.48}{760} \times \frac{273}{273 + 18} = 158.5 \text{ ml.}$$

The law of partial pressures applied to vapours is not exact ; the vapour pressure of a liquid in a gas is slightly *less* than *in vacuo*. It is only at low pressures, *i.e.* at low temperatures, when the vapour pressures are small, that the application is justified. This is very nearly the case at the ordinary atmospheric temperature.

Density of a moist gas.—Consider 1 litre of moist gas at t° , under a pressure P mm., and let p be the partial pressure of aqueous vapour in the gas. The volume of the *dry* gas at S.T.P. will be :

$$\frac{P-p}{760} \times \frac{273}{273+t} \text{ litres.}$$

Let the weight of 1 litre of dry gas at S.T.P. = D gm. The weight of the dry gas will be :

$$D \times \frac{P-p}{760} \times \frac{273}{273+t} \text{ gm.}$$

The volume of water vapour at S.T.P. will be :

$$\frac{p}{760} \times \frac{273}{273+t} \text{ litres.}$$

and since the (hypothetical) weight of 1 litre of aqueous vapour at S.T.P. is 0.8038 gm., the weight of vapour in 1 litre of moist gas will be :

$$0.8038 \times \frac{p}{760} \times \frac{273}{273+t} \text{ gm.}$$

The total weight of the litre of moist gas will therefore be :

$$\begin{aligned} D' &= D \times \frac{P-p}{760} \times \frac{273}{273+t} + 0.8038 \times \frac{p}{760} \times \frac{273}{273+t} \text{ gm.} \\ &= \frac{273}{(273+t)760} \{D(P-p) + 0.8038p\} \text{ gm.} \end{aligned}$$

The calculation applies to air, the appropriate density D being 1.2927. The equation will also give the density D of the dry gas at S.T.P. from the density D' of the moist gas.

EXAMPLE.—Find the weight of 1 litre of hydrogen, saturated with moisture at 15°, and under a pressure of 740 mm.

Normal density of hydrogen = 0.08987 gm. per litre ; vapour pressure of water at 15° = 12.79 mm., hence required weight

$$= \frac{273}{(273+15)760} \{0.08987(740-12.79) + 0.8038 \cdot 12.79\} = 0.09431 \text{ gm.}$$

Note that, whereas moist air is lighter than dry air, the reverse is the case with hydrogen. This is because aqueous vapour is lighter than air but heavier than hydrogen.

A similar type of calculation will give the density of any mixture of gases when the partial pressures, and the normal densities at S.T.P., are known.

Vapour densities.—Since vapours far from their points of liquefaction obey approximately the same laws of expansion as gases, the *normal density* may be found by dividing the weight of any volume of the vapour measured under the actual temperature and pressure of the experiment by the volume in litres corrected to S.T.P.

If the weight of V c.c. or ml. of vapour at a temperature t° and under a pressure of P mm. is m gm., the normal density is :

$$D = m \div \left\{ V \times 0.001 \times \frac{273}{273+t} \times \frac{P}{760} \right\} \text{ gm./lit.}$$

The vapour density of a volatile liquid or solid may be determined by one or other of the three following methods ; that selected depends on the conditions of experiment, e.g. whether a high or low temperature or pressure is used.

Hofmann's method.—In this method (A. W. Hofmann, 1868), a wide barometer tube, at least 1 metre long and graduated in ml., is surrounded with a glass jacket through which the vapour of a liquid boiling in a separate vessel is passed. Uniformity of temperature is thus assured. The vapour jacket is provided with a side tube near the bottom for leading the vapour to the condenser (Fig. 46). The liquid is weighed into a small bulb (Fig. 47) with a ground stopper, which is forced out when the bulb is passed into the upper vacuous part of the barometer tube and the liquid volatilises. The bulb must be completely filled with liquid, since a bubble of air will expand considerably in the vacuous space.

In Hofmann's method the volume of a given weight of vapour is determined.

When the mercury level is constant, the following data are noted :

- (i) The volume of the vapour in ml. = V .
- (ii) The temperature, t° , in the jacket.
- (iii) The pressure of the vapour : approximately given by the barometric height H mm., minus the height of mercury in the tube above the level in the trough, h mm. ; i.e. $(H - h)$ mm.

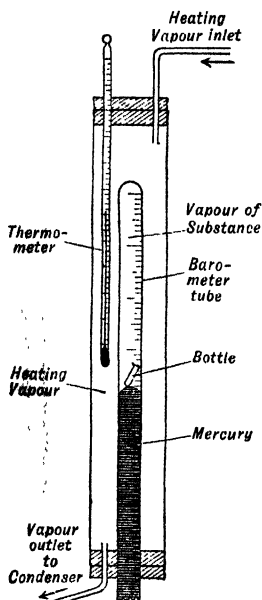


FIG. 46.—Hofmann's vapour density apparatus.

In accurate work, the height of the heated mercury in the column in the tube must be reduced to 0° to correspond with the corrected barometer reading, and allowance made for the volume of the bulb and the expansion of the scale of the glass tube. The vapour pressure of mercury at the temperature of the jacket is also subtracted from the pressure of the vapour.

Let the mass of substance taken be m grams. The volume of the vapour of the substance under the standard conditions is :

FIG. 47.—Bulb for liquid in vapour density determination.

$$V_n = V \times 0.001 \times \frac{273}{273 + t} \times \frac{H - h}{760} \text{ lit.}$$

The normal density is then m/V_0 .

EXAMPLE.—0.338 gm. of carbon tetrachloride gave 109.8 ml. of vapour in a Hofmann apparatus, at 99.5° . Barometric height = 746.9 mm. Height of mercury in tube above level in trough = 283.4 mm.

$$\therefore V_0 = 109.8 \times 0.001 \times \frac{273}{372.5} \times \frac{746.9 - 283.4}{760} \text{ lit.}$$

\therefore normal density of carbon tetrachloride = $0.338/V_0 = 6.884$ gm./lit.

The following liquids may be used for the vapour-jacket : the boiling points at 760 mm. pressure are stated :

Water, 100°.	Toluidine, 202°.
Amyl alcohol, 131°-132°.	Ethyl benzoate, 212·9°
Xylene, 140°	Amyl benzoate, 262°.
Aniline, 184·4°.	Diphenylamine, 310°.

Since volatilisation occurs more readily under reduced pressure, steam may often be used in the jacket for liquids which boil under full atmospheric pressure as high as 180°. If the atmospheric pressure during the experiment differs appreciably from 760 mm., the boiling point of the liquid furnishing vapour to the jacket must be corrected, or a thermometer hung in the jacket.

Dumas' method.—The method invented by Dumas (1826) is an extension of that commonly used for permanent gases, and the mass of a given volume of vapour is determined. Since the vapour does not come in contact with mercury, the method may be used with substances (*e.g.* bromine) which cannot be dealt with by Hofmann's method, and it may also, by the use of porcelain globes, be used at higher temperatures. It is not so accurate as Hofmann's method, and as vaporisation is carried out under atmospheric pressure, and the temperature of the vapour is higher, it cannot be used for substances which readily decompose.

In Dumas' method a thin glass bulb (Fig. 48) of about 150-200 ml. capacity, with a drawn-out neck, is cleaned, dried, and weighed. By warming the bulb, dipping the neck in the liquid, and cooling, sufficient liquid is introduced into the bulb to expel all the air when it is volatilised.

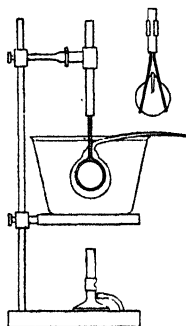


FIG. 48.—Dumas' vapour density apparatus.

Reproduced from Palmer's *Experimental Physical Chemistry*, (C.U.P.).

The bulb is held in a wire spring-clip in a wooden handle, and immersed in a pot containing water, oil, or melted paraffin wax, heated 30°-40° above the boiling point of the liquid, so that the tip of the neck projects above the surface of the liquid. Volatilisation occurs and the air is expelled from the bulb. When the evolution of vapour ceases, the neck of the bulb is sealed off, and the temperature of the bath read on a thermometer. The barometric pressure at the time of sealing is noted.

The bulb is removed from the bath, cooled, cleaned, and reweighed along with the piece of neck sealed off. The neck is scratched with a file, and the tip broken off under the surface of previously boiled water. The water enters the bulb and, if the experiment has been successful, fills it completely. The bulb full of water is weighed.

Let the weight of the bulb in air = m gm.

weight of the bulb filled with vapour = m_1 gm.

weight of the bulb filled with water = m_2 gm.

The volume of the bulb = $m_2 - m$ ml.

The weight of air filling the bulb at the temperature t , and pressure h , when it is weighed full of vapour, will be :

$$(m_2 - m) \times 0.001293 \times \frac{273}{273 + t} \times \frac{h}{760} \text{ gm.} = A \text{ gm.},$$

hence the weight of the vacuous bulb in air = $m - A$ gm., and the weight of vapour filling the bulb = $m_1 - (m - A)$ gm.*

The normal density of the vapour is :

$$[m_1 - (m - A)] \div 0.001(m_2 - m) \text{ gm./lit.}$$

In some cases the weight of vapour may be found by chemical methods. *E.g.* if iodine has been used, the tip of the bulb is broken off under potassium iodide solution, which dissolves the iodine, and the solution is then titrated with sodium thiosulphate.

EXAMPLE.—Weight of bulb filled with air = 65.50 gm.

Weight of bulb filled with vapour = 66.42 gm.

Temperature of weighing 15°, barometric pressure 745 mm., temperature of bath 248°.

Weight of bulb filled with water = 462.5 gm.

$$\therefore \text{ vol. of bulb at } 15^\circ = 462.5 - 65.5 = 397 \text{ ml.}$$

Vol. of air filling bulb at S.T.P. = $397 \times (745/760) \times (273/288) = 369 \text{ ml.}$

Density of air at S.T.P. = 0.001293 gm./ml.

$$\therefore 369 \text{ ml. of air at S.T.P. weigh } 0.4760 \text{ gm.}$$

Weight of vacuous bulb = $65.50 - 0.476 = 65.024 \text{ gm.}$

Weight of vapour filling bulb at 248° and 745 mm. pressure

$$= 66.42 - 65.024 = 1.396 \text{ gm.}$$

Vol. of this vapour at S.T.P. = $397 \times (273/521) \times (745/760) = 204 \text{ ml.}$

(The expansion of the bulb on heating is neglected).

Normal density of vapour = $1.396/0.204 = 6.84 \text{ gm./lit.}$

The chief drawbacks to Dumas' method are : (i) the large quantity of substance required to displace the air of the bulb ; and (ii) if the substance contains impurities of higher boiling point, these come off last and render the vapour sealed up impure, the density being too high.

Deville and Troost (1860) extended Dumas' method to higher temperatures by using bulbs of porcelain, heated in the vapours of mercury, sulphur, stannous chloride, cadmium, or zinc in an iron bath, and sealing off the tip of the bulb with an oxy-hydrogen blowpipe. To find the temperature of the bulb a companion globe filled with iodine, the density of which had been determined at various temperatures, was placed alongside the other bulb.

Victor Meyer's method.—In Victor Meyer's displacement method (1878), the volume of air displaced by a known mass of vapour is determined. It is more rapidly and easily carried out than the Dumas and Hofmann

* Strictly speaking, the density of atmospheric air containing some carbon dioxide and moisture should be used. According to Kohlrausch it is usually sufficient to take, as an average, the density at S.T.P. as 0.001295.

methods, requires only a small quantity of the substance, and gives quite accurate results.

A long glass tube with a bulb (Fig. 49) and a side tube is heated in a glass (or better, copper) vapour bath at a temperature which must be constant and about 30° higher than the boiling point of the substance, but need not otherwise be known. The side tube delivers into a graduated tube filled with water and inverted in a trough of water. The long tube is closed by a rubber stopper and heated in the bath until no more bubbles of air escape; then the side tube is placed under the graduated tube, the stopper at the top of the long tube is taken out, and a weighed quantity of the liquid in a small stoppered bulb is dropped into the heated bulb, the rubber stopper being quickly replaced. A little glass-wool or mercury is placed in the bottom of the bulb to prevent fracture on dropping in the bulb of liquid.

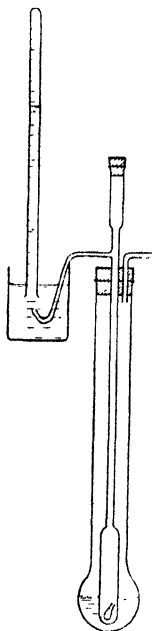


FIG. 49.—Victor Meyer's vapour density apparatus.

When no more bubbles come off, the tube is closed with the thumb, transferred to a tall cylinder of water, and the water levels are equalised. The volume of air is read off. This volume of air is equal to the volume which the vapour would occupy if it could be cooled from the temperature of the bulb to the atmospheric temperature.

Let the volume of moist air at the temperature t° of the water in the cylinder and under a barometric pressure H , be V ml. If the vapour pressure of water at t° is p mm., the volume of dry air at S.T.P. will be :

$$V_0 = V \times \frac{273}{273+t} \times \frac{H-p}{760} \text{ ml.}$$

This * is the volume which the vapour of the given weight of substance would occupy at S.T.P. if it could exist under these conditions, so that if m gm. of substance were used :

$$\text{normal density} = m / 0.001 V_0 \text{ gm./lit.}$$

EXAMPLE.—0.1008 gm. of chloroform expelled 20.0 ml. of moist air at 15° and 770 mm. pressure. Vapour pressure of water at $15^\circ = 13$ mm.

* The equation holds if the Victor Meyer tube was originally filled with dry air. If the partial pressure of water vapour in the air filling the tube at the beginning of the experiment was h , the factor $(H-p)$ becomes $(H-p+h)$. The difference in the result does not usually exceed the experimental error. The small volume of air displaced on inserting the rubber stopper is compensated by the displaced air which occupies the part of the delivery tube in the trough which originally contained water.

$$\therefore \text{volume of dry air at S.T.P.} = 20 \times \frac{273}{288} \times \frac{770 - 13}{760} = 18.9 \text{ ml.}$$

$$\therefore \text{normal density of chloroform vapour} = 0.1008/0.0189 = 5.33 \text{ gm./lit.}$$

Victor Meyer's method is not suitable for substances which decompose on heating, and decompose still further when the pressure is reduced (*e.g.* phosphorus pentachloride $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$), since, when the vapour mixes with air in the bulb, the partial pressure of the vapour is reduced to an extent which is not known.

Measurements by Victor Meyer's method at high temperatures were made by Nilson and Petterson (1889), and by Biltz and Victor Meyer, who used a bulb of glazed porcelain, protected by wrapping it with thick platinum foil, placed inside a graphite crucible heated in a Perrot's gas furnace. The bulb is filled with inert gas (nitrogen, or argon) to prevent chemical action, and the substance, weighed out in a glass bulb, is dropped in as usual. Nernst (1903) used a small iridium bulb (3 ml.), painted outside with zirconia, and heated electrically to 2000° in a small iridium tube-furnace. The substance (a fraction of a milligram) was weighed on a micro-balance sensitive to 1,2000 mgm., and the displacement measured directly by the movement of a drop of mercury in the horizontal graduated side tube (Fig. 50).

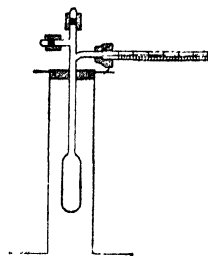


FIG. 50.—Nernst's apparatus for vapour densities at high temperatures.

CHAPTER VI

SOLUTIONS

Solutions.—Solid sugar or salt when added to water dissolves and forms a homogeneous solution. Liquid alcohol and water mix in all proportions to form solutions. It is generally possible, by suitable means, to separate the constituents of solutions, one method being by distillation. In this, the solution is heated and the vapour of the volatile liquid is condensed by cooling. Non-volatile substances (salt

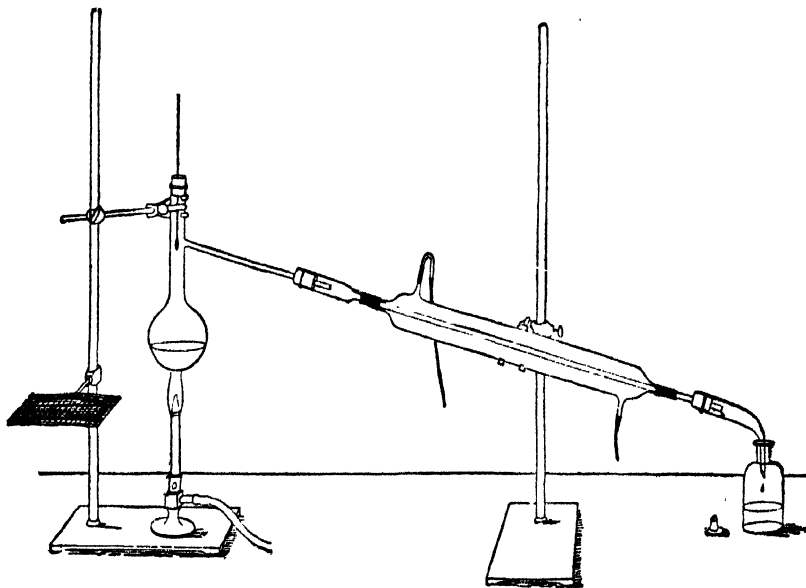


Fig. 51.—Distilling apparatus with Liebig's condenser.

or sugar) remain in the residual solution, or form a solid residue. This method of separation uses differences in vapour pressure of the components of a solution, at the same temperature.

A simple apparatus for distillation consists of a retort with the neck passing into a glass flask or receiver, which is cooled by a stream of cold water. If tap-water is distilled in this apparatus, mineral matter remains in the retort and distilled water collects in the receiver. When larger quantities of a liquid are distilled it is convenient to use a Liebig's condenser (Fig. 51), consisting of a glass tube enclosed in a jacket through which a stream of cold water is passed. The liquid to be distilled is contained in a distilling flask, with a side tube passed through a cork in the condenser. In the neck of the distilling

flask a thermometer is supported by a cork, so as to enable the boiling point of the liquid to be determined.

It is also possible by distillation to separate, at least partially, solutions of liquids in liquids. When a mixture of equal volumes of alcohol (b. pt. 78.3°) and water (b. pt. 100°) is distilled, the boiling point at the start is 84° . The liquid collecting in the receiver is richer in alcohol than the first mixture, and will burn when lighted in a dish. As distillation goes on the boiling point rises and the distillate becomes richer in water. If distillation is stopped when one-fourth of the mixture has passed over and the boiling point has risen to 85.5° , and if the distillate is poured into a clean flask and the operation repeated, the liquid begins to boil at 81.5° , *i.e.* at a lower temperature than the original mixture, and the first part of the distillate is richer in alcohol. This partial separation of a solution of liquids by interrupted distillation is known as **fractional distillation**.

True solutions are *homogeneous* (p. 3), and the dissolved substance is in an extremely fine state of division. One gm. of eosin gives a distinct fluorescence (p. 4) to 1,000,000 ml. of water when examined in a strong light. Each ml. of the solution contains only 0.000,001 gm. of the dye, and since a volume of only 10^{-12} ml. can be examined under the microscope, this can contain only 10^{-18} gm. of dye.

Colloidal solutions such as that of arsenic trisulphide (p. 7), pass through filter paper and do not settle on standing; their heterogeneous character is shown by the ultra-microscope. Colloidal solutions stand between suspensions (separable by filtration) and true solutions (homogeneous even under the ultra-microscope). The radius of the particles of dissolved substance in a true solution is of the order of 10^{-8} cm.

The substance present in larger amount in a solution, or the one which has the same physical state as the solution, is called the **solvent**; the other substance is called the **dissolved substance** or the **solute**. A mixture of alcohol and water may be called a "solution of alcohol in water" or a "solution of water in alcohol," according as water or alcohol is in excess, but a very concentrated solution of sugar in water, containing more sugar than water, is always called a "solution of sugar in water," because water has the same physical state as the solution.

Solutions of gases in liquids.—If a flask and delivery tube are completely filled with tap water and the flask heated, bubbles of gas appear, which pass out of the delivery tube under water and will be found to be mainly air; such water contains dissolved gas.

Solids can also dissolve gases; palladium dissolves hydrogen (p. 51), forming a **solid solution**. Solids may also dissolve solids: if a piece of gold-leaf is pressed on a freshly-scraped piece of lead, the gold slowly penetrates into the lead, as may be proved by scraping off successive layers after a long time and analysing them.

Solutions of gases in liquids may be studied by the apparatus shown in Fig. 52, called an **absorptiometer**.

The gas is measured over mercury in the burette *A* and the volume reduced to S.T.P. Part of the gas is then passed into the absorption vessel *C*, the volume of liquid, *e.g.* water previously boiled to expel dissolved air,

remaining in contact with the gas being the original volume minus the volume run out. *A* and *C* are connected by a flexible lead tube. The gas is shaken with the liquid until the solution is saturated. The pressure is adjusted by the levelling tube *B*. The contraction in volume is then read off on the burette and corrected for the vapour pressure of the liquid, temperature and barometric pressure. In accurate experiments the vessel *C* must be immersed in a bath of water at constant temperature.

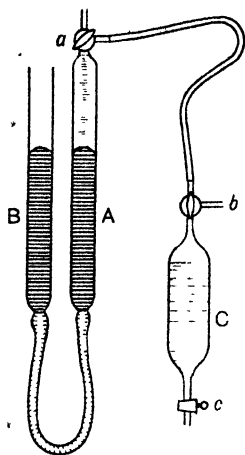


FIG. 52.—Absorptiometer.

If the gas is very soluble (e.g. ammonia, hydrochloric acid) it is passed into a measured volume of water until the latter is saturated. The amount of gas dissolved is then found by chemical analysis.

Bunsen's absorption coefficient β is the volume of gas reduced to S.T.P. which saturates 1 volume of liquid at a given temperature with the partial pressure of the gas equal to 1 atmosphere.

The amount of gas dissolved by a fixed volume of liquid depends on (1) the chemical composition of the gas and of the liquid, (2) the temperature, (3) the pressure. The effect of pressure is given by Henry's law (1803): *the amount of gas dissolved by a fixed volume of liquid at a given temperature is proportional to the pressure.*

Since the volume of a given amount of gas is inversely proportional to the pressure (Boyle's law) *a given volume of liquid dissolves the same volume of gas at all pressures.*

Ostwald's solubility coefficient λ is the volume of gas dissolved by 1 volume of liquid under the conditions of the experiment.

Let a volume V of liquid dissolve a volume v of gas at p mm. pressure and temperature t° . Then $\lambda = v/V$. Let α be the coefficient of expansion of the gas, then the volume of gas reduced to S.T.P. is

$$v_0 = v \times \frac{p}{760} \times \frac{1}{1 + \alpha t}$$

According to Henry's law, the volume of gas, measured at S.T.P., which is absorbed under a pressure of 760 mm. is $760/p$ times that absorbed under a pressure of p mm., viz. $760v_0/p = v/(1 + \alpha t)$. Bunsen's absorption coefficient is this divided by the volume of liquid V ,

$$\therefore \beta = v/V(1 + \alpha t) = \lambda/(1 + \alpha t).$$

Henry's law does not apply to very soluble gases, such as ammonia at the ordinary temperature, or hydrogen chloride, in water. It does not hold accurately for carbon dioxide. At 100° the solubility of ammonia (which is then very small) follows the law. At higher pressures deviations occur; with more soluble gases these begin at 2 atm. pressure, but with less soluble gases the law holds up to about 10 atm.

A few Bunsen's absorption coefficients are given below, in vols. at S.T.P. absorbed by 1 vol. of water at the given temperature, under a pressure of 760 mm. of dry gas (except for HCl, for which the total pressure of gas and water vapour is 760 mm.).

	0°	10°	15°	20°	30°	40°	50°	60°
Ammonia -	1300	910	802	710	—	—	—	—
Hydrochloric acid -	506	474	458	442	411	386	362	339
Carbon dioxide-	1.713	1.194	1.019	.878	.665	.53	.44	.36
Oxygen -	.049	.038	.034	.031	.026	.023	.021	.0105
Nitrogen -	.0239	.0196	.0179	.0161	.0138	.0118	.0106	.0100
Hydrogen -	.0215	.0198	.0190	.0184	.0170	.0164	.0161	.0160

Solubility of a mixture of gases in a liquid.—Dalton's extension of Henry's law states that: *the amount of any one gas dissolved from a mixture of gases is proportional to its partial pressure when the gas has come into equilibrium with the liquid.*

EXAMPLE.—The absorption coefficients of nitrogen, oxygen and argon in water at 0°, and the percentages by volume of these gases in dry air free from carbon dioxide, are given below. The partial pressures are proportional to the volume percentages:

Gas.	Percentage by vol.	Partial pressure (total 1 atm.)	Absorption coefficient.
Nitrogen -	78	0.78	0.0239
Oxygen -	21	0.21	0.0489
Argon -	1	0.01	0.053

By multiplying the partial pressures by the absorption coefficients, the volumes of the three gases dissolved in 1 vol. of water saturated with a large volume of air (constant composition) are found to be:

nitrogen, 0.01864; oxygen, 0.01027; argon, 0.00053; sum, 0.02944.

When the dissolved gas is expelled by boiling it will have this composition, or, expressed in percentages by volume it will contain:

$$\text{nitrogen } \frac{1.864}{0.02944} = 63.3; \text{ oxygen } \frac{1.027}{0.02944} = 34.9; \text{ argon } \frac{0.053}{0.02944} = 1.8.$$

The proportions of oxygen and argon have increased, since these gases are more soluble than nitrogen in water. By shaking water with an excess of this gas, the dissolved part when driven out will be still further enriched in oxygen, and so on. After eight repetitions the gas will contain over 90 per cent. of oxygen.

If the partial pressure of a gas above its solution can be reduced to zero, all the gas will be expelled. This can usually be done: (1) by reducing the pressure above the solution by an air-pump, (2) by passing a stream of indifferent gas through the solution (*e.g.* nitrogen through aqueous ammonia), or (3) by boiling the solution, when the dissolved gas is

driven off with the steam. When the gas and solvent evaporate *together* to form a vapour of the same composition as the solution, the solution evaporates as a whole, and no separation occurs (p. 211).

Solutions of liquids in liquids.—Some liquids, such as water and mercury, are practically though probably not absolutely *immiscible*; others, such as water and sulphuric acid, are *completely miscible*. In some cases, such as ether and water, each liquid dissolves a limited amount of the other, and the liquids are *partially miscible*. Small quantities of ether added to water at first dissolve completely. At a certain point, the water becomes saturated with ether; 100 gm. of water then dissolve 5.8 gm. of ether at 22°. If more ether is added, a lighter layer separates. This is not pure ether, but contains 4.12 gm. of water per 100 gm. of ether. On addition of more ether (if the layers are shaken together), the composition of each layer remains constant, but the lower (aqueous) layer gradually disappears and when it vanishes the whole liquid has the composition of the upper layer. Unlimited further quantities of ether may now be added without any separation of the liquid into layers.

The two liquid layers may be separated in a separating funnel (Fig. 7); the presence of ether in the lower layer may be shown by heating it in a test-tube, when the ether vapour given off may be kindled. The presence of water in the upper layer may be shown by dropping a bit of sodium into it, when hydrogen is evolved. (Pure ether has no action on sodium.)

The compositions of liquid layers in equilibrium at 22° is given below.

	Subst. in 100 gm. of water.	Water in 100 gm. of subst.
Ether - - - -	5.8 gm.	4.12 gm.
Chloroform - . -	0.62 „	0.10 „
Carbon disulphide -	0.218 „	10.81 „

The distribution law.—Iodine when shaken with chloroform and water dissolves in each, but the chloroform layer (as is seen from the colour) contains most of the iodine. Berthelot and Jungfleisch (1872) found that the weights of dissolved substance per unit volume of each liquid are in a constant ratio. This is called the *distribution* (or *partition*) *law*.

If c_1 , c_2 are the *concentrations*, or weights per unit volume, of the solute in the two layers, respectively, then :

$$c_1/c_2 = \text{const.} = k.$$

At 25° an aqueous solution of iodine containing 0.0516 gm. per litre is in equilibrium with a solution of iodine in carbon tetrachloride containing 4.412 gm. of iodine per litre. The *distribution coefficient* is :

$$\frac{\text{concentration in carbon tetrachloride}}{\text{concentration in water}} = \frac{4.412}{0.0516} = 85.5.$$

A saturated solution of iodine in water at 25° contains 0.340 gm. per litre. From the distribution coefficient the concentration of a solution of iodine in carbon tetrachloride, in equilibrium with a saturated solution in water, is found to be $0.340 \times 85.5 = 29.1$ gm. per litre.

Solutions of solids in liquids.—The most important solutions are those of solids in liquids. Common salt added in successive small amounts to water dissolves up to a certain point; after this no more salt passes into solution, but settles out unchanged. A solution which can exist in equilibrium with excess of solute under given conditions (e.g. at a fixed temperature) is called a saturated solution.

The **solubility** is the weight in grams of solid dissolved by 100 gm. of solvent at the given temperature, in presence of the solid salt. In the case of salts containing water of crystallisation (p. 180), the solubility is the weight of *anhydrous* salt (i.e. salt free from water) per 100 gm. of water in the saturated solution. The solubility depends (1) on the chemical characters of solute and solvent, (2) on temperature, and (3) to a slight extent on pressure.

The solubility usually increases with temperature. In a few cases, such as sodium chloride, it is nearly independent of temperature, and in others, such as sodium sulphate above 32.4° , it diminishes with rise of temperature.

Increase of pressure in some cases (sodium chloride) produces a slight increase, and in other cases (ammonium chloride) a slight decrease, in solubility.

Decrease of solubility with rise of temperature may be shown by placing a tube containing calcium butyrate solution, saturated at the ordinary temperature, in a beaker of hot water. In a short time crystals of the salt separate. They redissolve on cooling.

The dependence of solubility on temperature is represented graphically by solubility curves, in which abscissae represent temperatures, and ordinates solubilities (Fig. 53). The solubility always refers to equilibrium of the solution with a definite solid phase, e.g. a definite crystal hydrate.

Supersaturation.—When a saturated solution is cooled, the dissolved substance does not always separate from it. The cooled solution then contains more solute than corresponds with saturation at the given temperature, and is said to be *supersaturated*. Crystallisation is started by throwing a small crystal of solid into the solution.

Heat on a water-bath 250 gm. of crystal sodium thiosulphate ("hypo") in a flask, the neck of which is plugged with cotton-wool. The salt melts and dissolves in its water of crystallisation to form a very concentrated

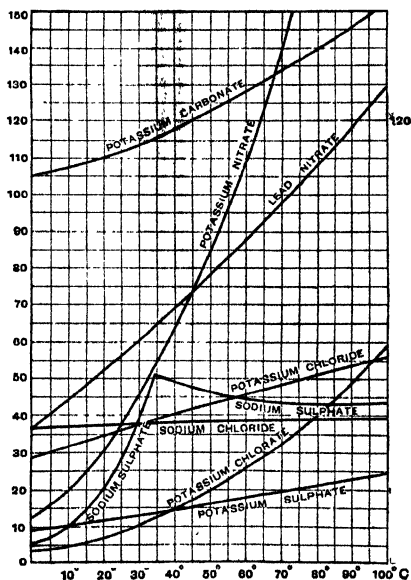


FIG. 53.—Solubility curves.

solution. On cooling this remains liquid and supersaturated. Remove the plug and drop in a crystal of hypo. The liquid begins to solidify, and the mass becomes warm, since heat is evolved.

Fuse some crystals of hypo in a long test tube, and pour over the liquid a supersaturated solution of sodium acetate, prepared by warming the crystallised salt with one-quarter its weight of water in a flask and filtering hot. Avoid mixing the liquids. Plug the tube with cotton wool and allow to cool. Remove the plug and drop in a crystal of hypo. This falls through the acetate solution without inducing crystallisation, but on reaching the hypo solution it causes crystallisation of the latter. Now drop in a crystal of sodium acetate. The upper liquid crystallises. Supersaturated solutions usually crystallise only by contact with the particular solid dissolved in them.

A supersaturated solution when strongly cooled may crystallise spontaneously, without contact with solid. If a supersaturated solution of hypo is cooled in a freezing mixture, it crystallises spontaneously.

Determination of solubility.—The solubility of a salt at various temperatures is determined by stirring the powdered solid salt with the solvent at the given temperature, so that excess of solid is present, withdrawing a portion of clear solution, weighing it, and then evaporating in a weighed dish to find the weight of solid salt contained in it.

An excess of powdered salt (*e.g.* potassium nitrate) is stirred with water at a constant temperature until the solution is saturated. The solution is allowed to settle and a portion withdrawn into a Landolt pipette (Fig. 54) by suction, the pipette is taken out, wiped, closed with pieces of glass rod and rubber tubing, cooled and weighed. The solution and any crystals are then washed out of the

pipette and the amount of solute determined either by evaporation in a weighed dish or by analysis.

An approximate solubility curve can be found by the *synthesis method*. A weighed amount of finely-powdered salt (*e.g.* KNO_3) is added to a known amount of water in a beaker until a little remains undissolved on stirring. The temperature is slowly raised until a mere trace of solid remains. The temperature is read. From the known weights of salt and water the solubility at that temperature is calculated. The temperature is then raised, a further weighed portion of salt is added, and the process described is repeated. In this way several points on a solubility curve are determined (Partington, *School Course of Chemistry*, p. 13).

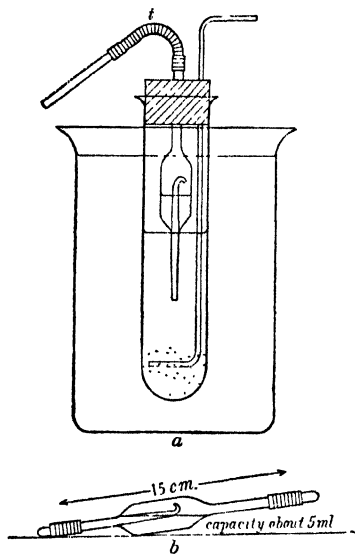


FIG. 54.—Determination of solubility of a solid in a liquid.

Reproduced from Palmer's "Experimental Physical Chemistry" (C.I.P.).

In the case of very sparingly soluble salts the data have been obtained by special methods, e.g. electrical conductivity (p. 232).

TABLE OF SOLUBILITIES

Salt.	0°.	15°.	100°.
Potassium iodide - - -	127.5	140	208
„ bromide - - -	53.5	62.5	104
„ chloride - - -	27.6	32.4	56.7
Sodium chloride - - -	35.7	35.9	39.0
Calcium chloride (CaCl ₂ , 6H ₂ O) -	60	100 (30°)	137 (60°)
Strontium chloride (SrCl ₂ , 6H ₂ O) -	43	50	—
Barium chloride (BaCl ₂ , 2H ₂ O) -	31.6	34.4	58.8
Potassium nitrate - - -	13.3	25.8	246
Sodium nitrate - - -	73.0	85	178
Barium hydroxide (Ba(OH) ₂ , 8H ₂ O)	1.67	2.23	101.4 (80°)
Calcium hydroxide - - -	0.185	0.70	0.077
Calcium sulphate (CaSO ₄ , 2H ₂ O) -	0.18	0.279 (40°)	0.260 (60°)
Strontium sulphate - - -	—	1.1 × 10 ⁻²	—
Barium sulphate - - -	—	2.8 × 10 ⁻⁴	—
Silver chloride	—	1 × 10 ⁻⁵	—
„ bromide - - -	—	1 × 10 ⁻⁵	—
„ iodide - - -	—	8.5 × 10 ⁻⁷	—

The freezing points of solutions.—When salt, sugar, or any soluble substance is added to water, the freezing point is lowered. *The lowering of freezing point is approximately proportional to the concentration of the solution.*

Sea water freezes at about -2° Bishop R. Watson in 1771 experimented with solutions of salt, exposing them to cold air “in equal quantities of water were dissolved quantities of sea salt, increasing in the arithmetical progression, 0, 5, 10, 15, 20, etc., the times in which the solutions began to freeze, reckoning from the time in which simple water began, increased accurately in the same progression hence it may be inferred, that, in salt of the same kind, the resistance to congelation is in the direct simple proportion of the quantity of salt dissolved this conclusion cannot be extended to salts of different kinds, since water saturated with sea salt is more difficultly congealed than when saturated with various other salts, which it dissolves in greater quantities”

Blagden in 1788 also found the lowering of freezing point proportional to the concentration.

The solid separating when solutions freeze is usually *pure ice*, the solute remaining in the unfrozen liquid. Freezing separates the constituents of a solution. The solution remaining becomes increasingly richer in salt as ice separates, and hence the freezing point falls.

A limit is reached when so much solvent has frozen out that the amount remaining in the liquid is only just enough to keep the salt in solution. On further cooling, ice and salt separate together in the same ratio as in the solution, and hence the temperature becomes constant, and the whole of the solution solidifies without further fall in tempera-

ture. This minimum temperature was formerly called the **cryohydric temperature**, and the mechanical mixture of ice and solid salt separating was supposed to be a compound and called a **cryohydrate** (Guthrie, 1875). Later experiments showed, by microscopic examination and in other ways, that cryohydrates are mechanical mixtures of ice and salt, and they are now called **eutectics**, the lowest temperature reached on freezing the solution being called the **eutectic point**.

Degrees of freedom.—The volume of a given mass of gas depends on temperature and pressure, but if any two of the three variables, pressure, volume, and temperature, are fixed, the third takes a definite value. Vapours behave similarly so long as no liquefaction occurs. The volume of a liquid or solid is fixed at a given temperature and pressure. It is convenient to consider the **specific volume**, or reciprocal of the density. The **state** of any homogeneous phase (gas, liquid, or solid) is definite when any *two* of the three variables, pressure, temperature, and specific volume, are fixed. This system of one phase ($P = 1$) is, therefore, said to have two **degrees of freedom** ($F = 2$), the number of degrees of freedom for any system being *the smallest number of independent variables defining the state which must be given definite values before this state is completely determined*.

A pure liquid can exist in equilibrium with its vapour only at one definite pressure (the vapour pressure) at a fixed temperature. The densities and states of both phases (liquid and vapour) are then completely determined. If the pressure is increased, some vapour condenses; if the pressure is reduced, some liquid evaporates. In both cases the pressure comes back to the equilibrium value. The system of water and ice behaves similarly: on increasing the pressure, some ice melts, and the original pressure is restored. A system of two phases of any pure substance has *one* degree of freedom ($F = 1$).

Ice, liquid water and water vapour coexist only at one temperature and one pressure, viz. $+0.0077^{\circ}$ and 4.57 mm.: these specify the **triple point** for water, at which three phases coexist ($P = 3$). In this case there is no degree of freedom ($F = 0$). The same is true for three coexisting phases of any pure substance.

Vapour pressures of solutions.—In the system of two phases of a pure substance in equilibrium, there is only one degree of freedom. If a little common salt be passed into a barometer tube containing water and water vapour, it dissolves in the water, and the vapour pressure is slightly lowered. The system of two phases, solution and vapour, in equilibrium has two degrees of freedom instead of only one in the case of pure water. The liquid phase is no longer a pure substance, but a solution of variable composition, the vapour pressure of which depends on the concentration of dissolved substance, which is an additional variable.

By adding more salt, the vapour pressure falls until the solution is just saturated with salt. The vapour pressure is again constant, since any more salt added remains undissolved. The extra phase, solid salt, reduces the number of degrees of freedom by one, since the pressure now depends on a single variable, temperature. With two components

(salt and water) in three phases ($P=3$) there is one degree of freedom ($F=1$).

To form a system of phases, some or all of which are solutions, or are pure substances not convertible into one another, a limited number of substances will be needed from which every phase may be formed. The number of components (C) is the least number of substances from which every phase in a system in equilibrium can be formed. Each of the three phases existing at the triple point of water can be composed of a single substance, water; systems formed from salt and water contain phases all of which can be formed of one or both of two components, salt and water.

The phase rule.—Consider the following table, which summarises results previously described. C denotes the number of components, P the number of phases, and F the number of degrees of freedom.

Equilibria	C	P	F
Water (liq.) \rightleftharpoons Water (vap.)	1	2	1
Water (solid) \rightleftharpoons Water (vap.)	1	2	1
Water (solid) \rightleftharpoons Water (liq.)	1	2	1
Water (solid) \rightleftharpoons Water (liq.) \rightleftharpoons Water (vap.)	1	3	0
Salt (dissd.) \rightleftharpoons Salt (solid)	2	2	2
Water (in sol.) \rightleftharpoons Water (vap.)	2	2	2
Water (in sol.) \rightleftharpoons Water (vap.) Salt (dissd.) \rightleftharpoons Salt (solid) }	2	3	1

In all cases the same simple relation exists between the number of phases P , of components C , and of degrees of freedom F , viz.,

$$\text{number of phases} + \text{number of degrees of freedom} = \text{number of components} + 2$$

$$P + F = C + 2.$$

This relation is general, and applies to all heterogeneous systems in equilibrium; it is called the phase rule and was deduced by J. Willard Gibbs in 1876.

Examples on the phase rule.—The following examples of applications of the phase rule are recapitulated.

1. Pure substance: $C=1$.

(a) Homogeneous gas, liquid, or solid: $P=1$, hence $F=1+2-1=2$.

Temperature and pressure, or temperature and concentration (density), or pressure and concentration, must be fixed before the state of equilibrium is defined.

(b) Coexisting phases of a pure substance: $C=1$.

(i) Solid \rightleftharpoons Liquid, or Solid \rightleftharpoons Vapour, or Liquid \rightleftharpoons Vapour. $P=2$, hence $F=1+2-2=1$, i.e. only temperature, or pressure, or one concentration, can be arbitrarily fixed before the state of equilibrium is completely defined.

(ii) Solid \rightleftharpoons Liquid \rightleftharpoons Vapour, i.e. the triple point. $P=3$, hence $F=1+2-3=0$, i.e. no single variable can be changed without causing complete disappearance of one phase from the system.

ture. Solutions, say of two components: $C = 2$.

- ter (a) Gas \rightleftharpoons Gas (dissd). $P = 2$, hence $F = 2 + 2 - 2 = 2$, i.e. temperature and pressure (or one concentration) only can be fixed, and the system is then in equilibrium. Henry's law gives a simple proportionality between pressure and concentration, but this holds only approximately.
- (b) Solid \rightleftharpoons Solid (dissd) $P = 2$, hence $F = 2 + 2 - 2 = 2$, i.e. the solubility depends on temperature and pressure. The effect of pressure, which is slight, is predicted by the phase rule.
- (c) Solid \rightleftharpoons Solution \rightleftharpoons Vapour of Solvent $P = 3$, hence $F = 2 + 2 - 3 = 1$, i.e. at a given temperature a solution can be in equilibrium with solid and vapour only at a definite pressure (the pressure of the saturated vapour), and concentration (that of the saturated solution).
- (d) Liquid I \rightleftharpoons Liquid II, two partly miscible liquids, say ether and water, existing in two layers in absence of vapour. $P = 2$, hence $F = 2 + 2 - 2 = 2$, i.e. the composition of each layer is fixed at a given temperature and pressure. The influence of pressure is small and is wholly eliminated if vapour is present: $P = 3$, hence $F = 2 + 2 - 3 = 1$, i.e. the miscibility depends only on the temperature.

The eutectic point, the freezing points of solutions, and the effect of adding iodine to two layers of ether and water, may be considered by the reader. The phase rule is seen to be at the same time general, simple, and capable of wide application.

compounds containing a metal atom with OH called hydroxyl, (see p. 180). Hydroxides of the oxides of calcium and other earths.

CHAPTER VII

ACIDS, BASES AND SALTS (caustic potash, caustic lime);

General properties of acids and bases.—One of the objects of chemistry is to arrange substances into groups of substances which have certain properties in common. Three important groups are acids, bases and salts.

Common acids met with in the laboratory are sulphuric, hydrochloric and nitric; and caustic soda, caustic potash, ammonia and lime are common examples of bases. The best known salt is common salt, but others such as nitre (or saltpetre), Glauber's salt (sodium sulphate) and Epsom salt (magnesium sulphate) are well known. Soda, potash and ammonia are examples of alkalis; all alkalis are bases, but there are bases such as lime which are not alkalis.

Since acids, alkalis and salts are easily differentiated by their common properties they were recognised as three groups of substances fairly early in the study of chemistry.

Boyle in his *Experimental History of Colours* (1664) recognised the following general properties of acids:

- (1) They have a sour taste.
- (2) They act as solvents but with varying power on different bodies; the varying strength of acids was recognised by Tachenius in 1666.
- (3) They precipitate sulphur from a solution of liver of sulphur (polysulphides of potassium).
- (4) They turn red many blue vegetable colours (e.g. litmus), the blue colour being restored by alkalis.
- (5) They react with alkalis, the characteristic properties of each substance disappearing and a neutral salt being formed.

On the basis of these, Hoffman (1723) and Black (1755) were able to show that carbonic acid is a true acid, though a weak one.

(6) Cavendish in 1766 showed that hydrogen gas is evolved by the action of sulphuric and hydrochloric acids on zinc, iron and tin.

Examples of alkaline substances, viz. slaked lime, plant and wood ashes and *natron* (native sodium carbonate found in Egyptian lakes) were known to the ancients. Pliny mentions the *caustification* of alkalis by boiling with quicklime as known in Egypt. The alchemists were acquainted with ammonium carbonate as *spirit of hartshorn*, prepared by the distillation of horn and bones or the putrefaction of urine. Later the names *mild alkali* and *caustic alkali* were introduced for the alkali before and after treatment with quicklime.

ture. ^{soluble, say of two parts} the following were recognised :
 (2) Gas \rightleftharpoons Gas (dissolved) and pressure (of the skin.)
 system is the blue colour of litmus reddened by acids and turn
 holds only

(3) ^{acidic} acids to form salts.
 (4) Solid \rightleftharpoons varieties effervesce with acids, giving off a gas which
 was insoluble, Black in 1755 and called by him "fixed air" (carbon
 dioxide).

Potash and soda were distinguished from one another by Duhamel in 1736 and by Marggraf in 1757.

Neutralisation.—When solutions of an acid and an alkali are mixed in the correct proportions the resulting solution has no acid or alkaline character and on evaporation it gives a solid salt. This reaction is called neutralisation because the product has neither acid nor alkaline properties (Latin, *neuter*, neither).

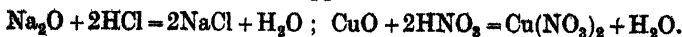
Neutralisation is an example of the quantitative aspect of chemistry ; acid and alkali react to form a salt in fixed ratios which are not the same for different acids and bases.

The names of acids, bases and salts.—Some acids, e.g. hydrochloric acid HCl, do not contain oxygen and the names of their salts end in *-ide*, e.g. sodium chloride (NaCl),* potassium cyanide (KCN). Many acids contain oxygen and are called *oxyacids*, e.g. sulphuric acid H₂SO₄ and nitric acid HNO₃. All acids contain hydrogen. The terminations *-ous* and *-ic* are used to distinguish oxyacids containing less or more oxygen combined with the same elements, the terminations *-ite* and *-ate* being used for the corresponding salts :

ACID.	SALT.
Sulphurous H ₂ SO ₃ .	Sodium sulphite Na ₂ SO ₃ .
Sulphuric H ₂ SO ₄ .	Copper sulphate CuSO ₄ .
Nitrous HNO ₂ .	Potassium nitrite KNO ₂ .
Nitric HNO ₃ .	Lead nitrate Pb(NO ₃) ₂ .

Oxides forming acids with water are called **acidic oxides**, or sometimes **acid anhydrides** (Greek, *a* without, *hudor* water).† The acid anhydrides are now called by their systematic names, e.g. sulphur dioxide (SO₂), nitrogen pentoxide (N₂O₅), etc.

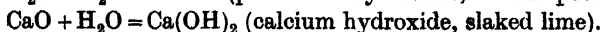
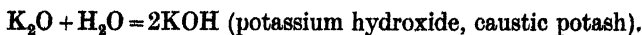
Oxides forming salts and water with acids are called **basic oxides**. E.g. sodium oxide Na₂O, and copper oxide CuO :



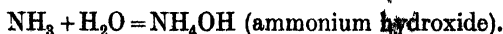
* In the following sections a knowledge of chemical formulae and equations is assumed ; see Chapter VIII.

† The distinction between "anhydride" and "anhydrous substance" (one free from water) should be noticed.

Some basic oxides form with water compounds containing a metal (or radical, *cf.* below) united with a group of atoms OH called *hydroxyl*, and are therefore called *hydroxides* (not "hydrates"; p. 180). Hydroxides of sodium and potassium are called *alkalis*; the *oxides* of calcium, strontium and barium were formerly called *alkaline earths*.



We may suppose that ammonium hydroxide is formed when ammonia gas dissolves in water, since the liquid is alkaline:

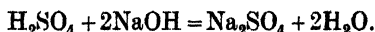


Acidic and basic oxides *combine* to form salts:

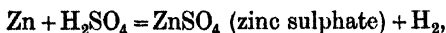


In the old *Dualistic System* of Berzelius salts were regarded as containing the basic and acidic oxides, called "electropositive" and "electro-negative" respectively: sulphate of soda $\text{Na}_2\text{O}.\text{SO}_3$. This notation still has its uses in balancing equations of oxidation reactions, potassium permanganate being written $\text{K}_2\text{O}.\text{Mn}_2\text{O}_7$, and potassium dichromate $\text{K}_2\text{O}.2\text{CrO}_3$, ferrous sulphate $\text{FeO}.\text{SO}_3$, and ferric sulphate $\text{Fe}_2\text{O}_3.3\text{SO}_3$.

Acids and bases *react* to produce salts and water:

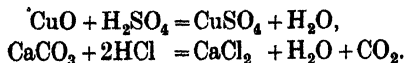


The salt Na_2SO_4 may be regarded as sulphuric acid H_2SO_4 in which two atoms of hydrogen are replaced by two atoms of metal. This may take place directly, as when zinc dissolves in dilute sulphuric acid:



or indirectly when the acid is neutralised by a base.

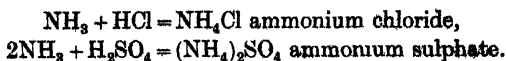
Salts are also formed by the action of acids on basic oxides, hydroxides, and carbonates; with carbonates gaseous carbon dioxide is evolved with effervescence:



Besides *acidic* and *basic oxides*, there are *neutral oxides* (not forming acids or bases with water, *e.g.* nitric oxide NO, and carbon monoxide CO), *amphoteric oxides* (behaving at the same time as weak acids and weak bases, *e.g.* aluminium oxide), *peroxides* (higher oxides, containing much oxygen: see p. 197), and *double oxides* (composed of two oxides, *e.g.* ferrous-ferric oxide composed of ferrous oxide and ferric oxide: $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$).

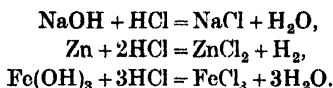
Radicals.—Sometimes a *group of atoms* plays the part of a single atom and occurs in a whole series of compounds. The salts formed by the

combination of ammonia with acids all contain the group NH_4 , which plays the part of a metal and is called ammonium :

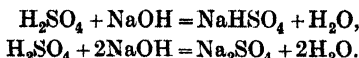


*An unvarying group of atoms present in a series of closely related compounds is called a radical (Latin, radix, a root). The group OH (hydroxyl) in hydroxides, the group SO_4 in sulphuric acid and sulphates, and the group NO_3 in nitric acid and nitrates, are radicals.**

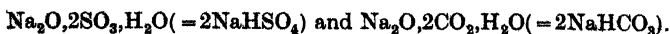
Normal, acid, and basic salts.—When the molecule of an acid contains only one atom of hydrogen which can be replaced by a metal it forms only one class of salts. *An acid containing in its molecule only one atom of hydrogen which can be replaced by a metal or radical to form a salt is called a monobasic acid:*



An acid containing in its molecule two atoms of hydrogen which can be replaced by a metal or radical and can form two classes of salts is called a dibasic acid. Sulphuric acid H_2SO_4 is dibasic. Either one atom of hydrogen can be replaced by a metal (or ammonium) to form an acid salt or both atoms can be replaced to form a normal salt :

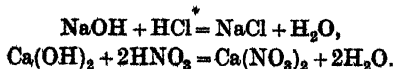


The names sodium hydrogen sulphate, etc., are now generally used instead of acid sodium sulphate, etc. The name "normal" is never used in speaking of salts individually: we say simply "sodium sulphate," etc. Sometimes acid salts are called *bisulphate, bicarbonate*, etc., from the old formulae :



A base containing in its molecule one, two, etc., hydroxyl radicals which it loses on reaction with an acid to form salts is called a monacid, diacid, etc., base.

Sodium hydroxide is a monacid base, calcium hydroxide is a diacid base :

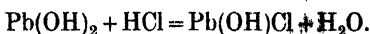


* In qualitative analysis the constituents of salts, viz. metals and ammonium and acid radicals, are often called "radicals", a mixture of calcium phosphate and ammonium sulphate "contains four radicals". The spelling "radical" is now preferred to "radicle".

These names are used also for organic bases which combine directly (like ammonia) with acids to form salts :



Basic salts may be regarded from two points of view. Bases contain hydroxyl OH, which reacts with the acidic hydrogen of acids to form water, and the other atom or radical of the base then forms a salt with the radical of the acid. When a base contains more than one hydroxyl group a salt may be formed which still contains one or more hydroxyl groups of the base :



We call $\text{Pb}(\text{OH})\text{Cl}$ lead hydroxychloride or basic lead chloride. Basic salts rarely have simple formulae such as this, and it is usual to regard them as compounds of normal salts with the free base or basic oxide. Thus the common basic lead chloride is $\text{PbCl}_2 \cdot 7\text{PbO}$, and a basic copper carbonate is $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$.

LIME AND THE ALKALIS

Black's researches on the alkalis.—The chemical nature of chalk and lime and of the alkalis was largely explained by the classical researches of Joseph Black (1754–6). In his time three alkalis were known, each in two forms, a mild and a caustic (obtained by boiling with lime) :

(1) Mild vegetable alkali (potassium carbonate K_2CO_3) obtained from plant ashes; caustic vegetable alkali (potassium hydroxide KOH).

(2) Mild marine (or mineral) alkali (sodium carbonate Na_2CO_3) obtained from ashes of plants growing on the sea shore (deep-sea weeds contain the vegetable alkali); caustic marine alkali (sodium hydroxide NaOH).

(3) Mild volatile alkali, containing ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$, obtained by the distillation of bones, from putrefied urine or from *sal ammoniac*; caustic volatile alkali (ammonium hydroxide NH_4OH , described by Boyle in 1675).

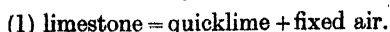
Limestone, chalk and marble are varieties of calcium carbonate CaCO_3 . On strong heating ("burning"*) it forms quicklime which is strongly basic and is appreciably soluble in water to form an alkaline solution (lime water).

Before Black's work it was thought that limestone on burning took up a "principle of causticity" from the fire, becoming quicklime, and that this principle was transferred to a mild alkali on boiling with quicklime, thus rendering the alkali caustic.

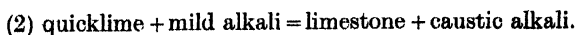
Black (who worked chiefly with magnesia) found that when limestone is heated there is a loss of weight, and a gas which he called "fixed air"

* "Burning" is not a very accurate description of the preparation of lime, since combustion of the limestone does not take place, but it is the correct technical name for the process.

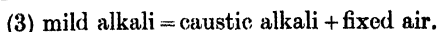
(CO₂, overlooked in the old theory) is evolved. The residue is quicklime :



If the quicklime is slaked and boiled with a solution of mild alkali, the alkali becomes caustic and the quicklime is converted into the original weight of limestone :



If we add equation (1) to equation (2) we find :



So far from quicklime and caustic alkalis being compounds of limestone and mild alkalis with some caustic principle, they are seen to be simpler than the mild forms, and the mild forms part with fixed air in producing the caustic forms. Hence, according to Black, the corrosiveness of quicklime and caustic alkali is an essential property of the pure earth and the pure alkali, respectively, and is not due to any separate principle of causticity. Black also remarked that :

“ when we mix an acid with an alkali [*i.e.* a *mild* alkali], or with an absorbent earth [limestone or chalk], [fixed] air is set at liberty and breaks out with violence; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time.”

When the solution of limestone in acid is mixed with mild alkali the original weight of limestone is precipitated. In this case no fixed air is evolved from the mild alkali although the latter forms a salt with the acid. This is because the fixed air is transferred to the lime with the formation of limestone. The theory of caustification is thus stated by Black :

“ If quicklime be mixed with a dissolved alkali, it likewise shows an attraction for fixed air, superior to that of the alkali. It robs this salt of its air, and thereby becomes mild itself; while the alkali is consequently rendered more corrosive, or discovers its natural degree of acrimony, or strong attraction for water; which attraction was less perceivable, as long as it was saturated with air. And the volatile alkali [ammonium carbonate], when deprived of its air, besides this attraction for various bodies, discovers likewise its natural degree of volatility [as ammonia gas], which was formerly somewhat repressed, by the [fixed] air adhering to it, in the same manner as it is repressed by the addition of an acid.”

The action of heat on marble.—The evolution of “fixed air” on heating limestone (or marble) may be shown by the following experiment.

Some powdered marble is *strongly* heated in a hard glass tube and a slow stream of heated air is drawn by an aspirator over the marble, then bubbling through lime water in a test-tube (Fig. 55). The lime water becomes milky. This is a characteristic property of carbon dioxide, hence marble

on heating decomposes into quicklime and carbon dioxide. (Since the pressure of carbon dioxide over heated marble does not reach atmospheric pressure below a *bright red* heat, it is necessary to sweep away the gas by a current of air). The residue in the tube, on cooling, will turn moist red litmus paper blue.

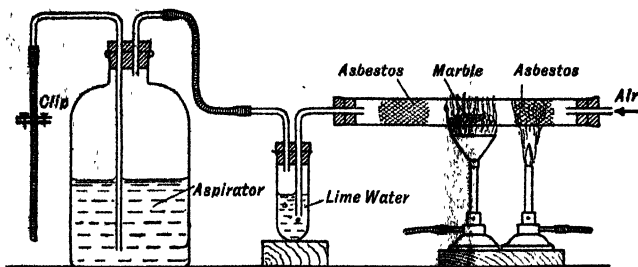


FIG. 55.—Decomposition of marble by heat.

The action of acid on marble.—The weight of carbon dioxide given off from chalk or marble on treatment with acid may be found with the apparatus shown in Fig. 56.

The flask is fitted with a tube tightly packed with cotton wool to keep back spray; the test-tube inside contains 1 gm. of marble and the flask contains 20 ml. of concentrated hydrochloric acid diluted with its own volume of water. The tube containing the marble is supported by a piece of fine thread passing outside as shown, and the apparatus is weighed.

The rubber stopper is loosened and the tube containing the marble allowed to drop into the acid. The stopper is then quickly and tightly replaced. The marble is allowed to dissolve in the acid.

Since the flask is now filled with carbon dioxide which is heavier than air, this gas must be displaced by aspirating a slow stream of air through the tube fitted with the clip, which was previously kept closed. The clip is again closed and the apparatus weighed. The loss in weight represents the carbon dioxide evolved from 1 gm. of marble. One gram of marble should give 0.44 gm. of carbon dioxide.

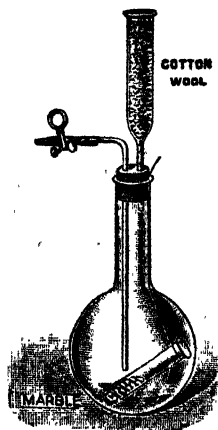


FIG. 56.—Decomposition of marble by acid.

The action of quicklime on mild alkali.—The reaction in the caustification of mild alkali (washing soda) by quicklime is shown in the following experiments.

(1) A piece of pure quicklime (from marble) is weighed and is slaked with water in a porcelain dish. The thin paste is boiled for some time with an excess of washing soda solution. The liquid is diluted with hot distilled water and filtered through a weighed filter paper (the concentrated solution

disintegrates filter paper), the precipitate being well washed with hot water. It is then dried and weighed.

The powder on the filter paper is an artificial marble or limestone, which will effervesce with acid. One gram of limestone should be obtained from 0.56 gm. of quicklime, and 1 gm. of marble has been found to contain 0.44 gm. of carbon dioxide. But $0.56 \div 0.44 = 1.00$, hence the marble contains only quicklime and carbon dioxide.

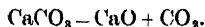
(2) An excess of slaked lime is boiled with a solution of washing soda (best in an iron pan). The clear solution when decanted is found to have become caustic (soapy feel; action on red litmus; no, or only slight, effervescence with acid). On evaporation in a dish a fused mass of caustic soda may be obtained and, as Black found:

"having once evaporated a part of the . . . ley in a bowl of English earthen or stone ware, and melted the caustic with a gentle heat, it corroded and dissolved a part of the bowl, and left the inside of it pitted with small holes." A silver dish should be used, he says, but an iron one, *e.g.* a sand bath, is fairly satisfactory.

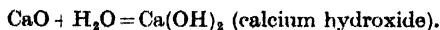
The action of mild alkali on "lime salt".—When a known weight of marble is dissolved in hydrochloric acid, carbon dioxide is evolved with effervescence. The solution formed gives on evaporation a deliquescent salt called calcium chloride, and the same "lime salt" is produced from quicklime and hydrochloric acid but in this case no gas is evolved. By mixing the calcium chloride solution with washing soda, a white precipitate is formed which when filtered, washed and dried, is found to be limestone. The weight of this should equal the weight of marble originally taken. The filtrate from the limestone precipitate when evaporated gives common salt, and this is also produced by the action of hydrochloric acid on either washing soda or caustic soda.

The reactions in Black's experiments can be represented by the following equations:

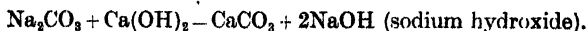
1. Preparation of quicklime (calcium oxide) from limestone (calcium carbonate):



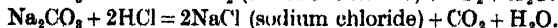
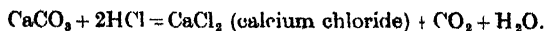
2. Slaking of lime:



3. Caustification of mild alkali (sodium carbonate):



4. Action of acid on limestone or mild alkali:



5. Precipitation of lime salt (calcium chloride) by mild alkali:



An important feature of Black's work which was mentioned on p. 12 was the use he made of quantitative experiments. He was not the first to use the balance in chemical experiments, since Boyle had done this,

but Black's method drew the attention of chemists to the need for quantitative experiments, and Lavoisier (who knew Black's work well and was much influenced by it) was able to make great progress in chemistry by his constant use of the balance: When Lavoisier proved, for example, that a metal gains in weight when it is converted into a calx, and an equal weight of air disappears, it could no longer be said that the change is due to the escape of phlogiston (p. 32). Before this, Black had shown that when limestone is converted into quicklime on heating, its weight decreases, so that it cannot gain a fiery matter in becoming caustic but must lose something, which Black showed was a peculiar gas, fixed air.

CHAPTER VIII

THE LAWS OF CHEMICAL COMBINATION AND THE ATOMIC THEORY

It was seen in Chapters II–IV that progress was made when chemical changes were studied *quantitatively*, and as a result of such experiments five general laws were discovered. These are :

- (1) The Law of Conservation of Mass.
- (2) The Law of Constant Proportions, or the Law of Definite Proportions.
- (3) The Law of Multiple Proportions.
- (4) The Law of Reciprocal Proportions, or the Law of Equivalent Proportions.
- (5) The Law of Gaseous Volumes.

The first was discussed in Chapter II, and the Law of Gaseous Volumes will be studied in Chapter IX. The *explanation* of these laws is given by the Atomic and Molecular Theories, but the laws themselves are purely experimental and independent of theory.

The law of constant proportions.—This law was stated by Proust in 1797 : *elements combine in definite ratios by weight, so that the composition of a pure chemical compound is independent of the way in which it is prepared.*

“ We must,” says Proust in 1799 and 1806, “ recognise an invisible hand which holds the balance in the formation of compounds . . . a compound is a substance to which Nature assigns fixed ratios, it is, in short, a being which Nature never creates otherwise than balance in hand, *pondere et mensurâ.*”

Berthollet, a contemporary and acquaintance of Lavoisier, said in his *Chemical Statics* (1803) that the composition of a compound was variable and depended on its mode of preparation. He relied on the following experimental evidence :

1. A metal such as lead when heated in air, absorbs oxygen in continuously increasing amounts up to a fixed maximum, corresponding with the formation of red lead.

2. A salt of a soluble acid and an insoluble base, such as sulphate of copper, may be precipitated with increasing amounts of a soluble base, such as potash, to form a continuous series of basic salts, in which the proportion of acid continuously decreases.

3. When mercury dissolves in nitric acid, it unites with quantities of oxygen varying continuously from a minimum, when it forms mercurous salts, to a maximum, when it forms mercuric salts.

4. Solutions of sulphuric acid, salts, alcohol, etc., metallic alloys, amalgams, and glasses, can have very variable compositions.

Proust met these objections by experiments :

(1) The supposed continuous series of metallic oxides are *mixtures* of two (or a small number) of oxides, each of definite composition. The oxides of tin obtained by calcining the metal in air are all mechanical mixtures of two definite oxides (possibly with some unchanged metal).

	1. Stannous oxide.	2. Stannic oxide.
Tin - - -	87	78.4
Oxygen - -	13	21.6

(2) The basic salts of copper of variable composition are mixtures of definite basic salts with hydrated oxide of copper.

(3) Mercury dissolving in nitric acid forms *only two* salts : mercurous nitrate with excess of metal and cold dilute nitric acid, and mercuric nitrate from the metal and excess of concentrated nitric acid. The other supposed salts are mixtures of these.

Berthollet had to recognise that substances of definite composition could very often be formed, but he regarded these as exceptional. In them, the proportions of the elements gave the compound which was least soluble, or most volatile, or densest. Thus, "it so happens that salts separate out by crystallisation in the neutral state, because in the neutral state the insolubility is greatest."

The fourth class mentioned by Berthollet gave Proust a good deal of trouble. He replied by pointing out the difference between a *pure substance* and a *solution*. He says :

"Is the power which makes a metal dissolve in sulphur different from that which makes one sulphide dissolve in another? I shall be in no hurry to answer this question, legitimate though it be, for fear of losing myself in a region not sufficiently lighted up by the facts of science ; but my distinctions will, I hope, be appreciated all the same when I say : The attraction which causes sugar to dissolve in water may or may not be the same as that which makes a fixed quantity of carbon and of hydrogen dissolve in another quantity of oxygen to form the sugar of plants, but what we do clearly perceive is that these two kinds of attraction are so different in their results that it is impossible to confound them."

In fact, the matter is not simple ; alloys are sometimes mixtures of the metals, each of which has crystallised out separately on cooling ; sometimes they are homogeneous solutions ; sometimes they contain definite compounds, and sometimes all of these states. Only the application of the Phase Rule has made it possible to decide to which class a particular alloy belongs. Proust was wise in refusing to be in a hurry to answer this question.

The exactness of the law of constant proportions seemed to be proved by experiments of Stas (1865). Marignac (1860) had suggested that very slight differences might occur in the composition of compounds made in different ways, but Stas's works seemed to show

that such differences do not exceed 1 part in 100,000, within the limits of experimental error.

Isomerism and allotropy.—The law of constant proportions states that a definite compound has a fixed chemical composition. The converse is not always true: the same elements may combine in the same proportions to form two or more different substances, each with characteristic properties. This is known as isomerism, and different substances of the same composition are called isomers. Chemical composition alone does not uniquely determine a pure substance.

Red mercuric iodide changes at 126° into a yellow form of identical composition. This remains yellow on cooling, but changes into the red form when rubbed.

An element may exist in various forms, which are called **allotropic modifications**, or **allotropes**. Allotropy is one form of isomerism. (The name allotropy is now frequently applied to compounds in different physical states, such as the two forms of mercuric iodide, as well as to forms of elements). Examples of allotropy are the forms of sulphur (p. 450), phosphorus (p. 568), and carbon (p. 593).

Isotopes.—Soddy and Hyman in 1914 found that specimens of lead chloride, prepared respectively from thorium and uranium minerals containing lead, differ in composition by 1 part in 225. This was confirmed by Richards and Lambert (1914). There are different varieties of lead, which combine in different proportions with chlorine. The different varieties of an element, which have different combining proportions, are called **isotopes**.

Some results giving the weights of different specimens of lead from minerals, which combine with 70.92 parts of chlorine, are given below. The first three minerals are all varieties of pitchblende, uranium minerals free from thorium; the last two are thorium minerals containing also some uranium. The value for ordinary lead is 207.2.

{ East African pitchblende - - - - -	206.05
{ Bröggerite - - - - -	206.06
{ Cleveite - - - - -	206.08
{ Thorianite (containing also 26.8 per cent. uranium) - -	206.83
{ Thorite (30.1 per cent. thorium; 0.45 per cent. uranium) -	207.90

It will be explained later that many ordinary elements are mixtures of isotopes. Since (1) these mixtures are usually inseparable by ordinary chemical means, and (2) all specimens of the element usually contain the isotopes in the same ratios, the element behaves in chemical changes as a single substance. It is only by special methods that isotopes can be separated, although in one or two cases, as in the varieties of lead, different natural specimens have different combining weights. Ordinary chlorine is a mixture of two isotopes, sodium is a single element, yet all specimens of common salt so far examined have been identical in composition, the isotopes of chlorine in them being always present in the same ratio.

The law of multiple proportions.—As a result of some theoretical speculations, John Dalton about 1803 concluded that: *when two*

elements combine to form more than one compound, the weights of one element which unite with identical weights of the other are in the ratio of whole numbers, usually small.

Although Proust knew of different oxides and sulphides of tin, copper, and iron, his analyses were not accurate enough to show any simple relation between the weights of oxygen or sulphur combined with identical weights of metal. In the two oxides of tin (p. 83), the weights of tin combining with 100 parts of oxygen are in the ratio 1 : 1.87. According to Dalton, the ratio should be exactly 1 : 2. Dalton's analyses were no more exact than Proust's, but those made later by Berzelius proved the accuracy of the law.

Dalton, by mixing 100 vols. of air with 36 vols. of nitric oxide over water in a narrow tube (5 in. \times 0.3 in), obtained a residue of 80 vols. of nitrogen, after all the oxygen of the air had combined with the nitric oxide to form red fumes, which were absorbed by the water. But if the experiment was performed in a wide cylinder, 72 vols., *i.e.* 36×2 vols. of nitric acid could be added, 80 vols. of nitrogen again remaining. Thus, "... oxygen can combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity."

Analyses of two oxides of carbon by Desormes, and of two hydrides of carbon by Dalton (1804), also confirmed the law :

	Carbon monoxide.	Carbon dioxide.
Carbon - - -	44	28.1 } or { 44
Oxygen - - -	56	71.9 } (112.6 = 56 \times 2.01
	Marsh gas.	Olefant gas.
Carbon - - -	4.3	4.3
Hydrogen - - -	2	1

A striking example of the law of multiple proportions is given by the five oxides of nitrogen. The weights of oxygen combined with 100 parts of nitrogen in these are as follows :

57 114 171 228 285

If all these numbers are divided by the least, 57, we obtain the series :

1 2 3 4 5

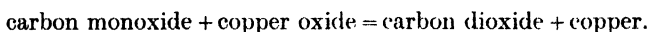
showing that the weights of oxygen combining with identical weights, 100 parts, of nitrogen to form the five compounds are in the simple ratios 1 : 2 : 3 : 4 : 5.

Weigh out two portions of 6.35 gm. of iodine. Add one in small quantities at a time to 10 gm. of mercury in a small mortar, triturating the contents after each addition of iodine. The mixture is converted into a *green* powder (mercurous iodide). To this add a further 6.35 gm. of iodine and triturate. A *reddish-yellow* powder (mercuric iodide) is formed. In mercuric iodide the same weight of mercury is combined with *twice* the amount of iodine contained in mercurous iodide.

Wrap 0.1 gm. of bicarbonate of potash in tissue paper and pass it to the top of a eudiometer filled with mercury, the upper part containing 1 ml. of concentrated hydrochloric acid. Carbon dioxide is evolved. Heat gently 0.2 gm. of bicarbonate in a crucible for a few minutes: it loses some carbon dioxide, forming carbonate of potash. With acid, this evolves the same volume of gas as the 0.1 gm. of bicarbonate. Hence the bicarbonate, on heating, loses exactly half its carbon dioxide in forming the carbonate.

The last experiment is due to Wollaston (1808); Thomas Thomson (1808) showed that oxalic acid reacts with potash in two proportions, producing a neutral and an acid salt, and the acid oxalate requires, for identical weights of potash, exactly twice as much acid as the neutral salt. Wollaston discovered a third oxalate and found the weights of oxalic acid to be in the ratios 1 : 2 : 4. The law of multiple proportions applies not only to elements, but also to compounds which interact chemically.

The exactness of the law was illustrated by Stas (1849). Carbon dioxide was prepared by passing oxygen over a weighed amount of pure charcoal, diamond, or graphite, heated in a tube, and the gas was absorbed in tubes containing potassium hydroxide. Carbon monoxide was also oxidised to dioxide by passing it over red-hot copper oxide:



One hundred parts of carbon dioxide contained 27.278 parts of carbon. The weight of carbon monoxide giving 100 parts of carbon dioxide was 63.640. Hence, 100 parts of carbon dioxide are produced from:

63.640 parts of carbon monoxide and $100 - 63.640 = 36.360$ parts of oxygen;

27.278 parts of carbon and $100 - 27.278 = 72.722$ parts of oxygen.

Again, 63.640 parts of carbon monoxide contain 27.278 parts of carbon and $63.640 - 27.278 = 36.362$ parts of oxygen. Thus 27.278 parts of carbon are combined in carbon monoxide with 36.362 parts of oxygen, and in carbon dioxide with 72.722 parts of oxygen. But $36.362 : 72.722 = 1 : 1.99995$, which differs from the exact ratio 1 : 2 by only 1 part in 40,000.

The law of equivalent proportions.—In 1766 Cavendish called a given weight of potash the *equivalent* of a (different) weight of lime when both neutralise identical weights of an acid. In 1788 he showed that the quantities of nitric and sulphuric acids which neutralise two identical weights of potash also decompose two identical weights of marble, different from those of the potash. This was the first clear recognition of equivalent weights of substances. In some experiments which he did not publish, Cavendish weighed out equivalent weights of salts, dissolved them in equal volumes of water, and compared the electrical conductivities of the solutions.

Experiments on the compositions of salts and the proportions in which they interact chemically, were made by C. F. Wenzel, and published in his *Lehre von der Verwandtschaft der Körper* (*Theory of the Affinity of Bodies*), Dresden, 1777. Berzelius, apparently by an oversight, said that Wenzel

discovered the law of equivalents. This is not confirmed by an examination of the book, which is written in an involved and obscure style.

In one experiment Wenzel discusses the reaction between silver chloride and mercuric sulphide, producing silver sulphide and mercuric chloride. From his analyses of the four compounds he concluded that the silver of the silver chloride would not be sufficient to combine with all the sulphur of the mercuric sulphide. The inference is that the excess of sulphur remains uncombined. In other cases, Wenzel actually refers to uncombined residues from double decompositions, and suggests that they be used up by adding other substances.

The generalisation of Cavendish's experiments is due to J. B. Richter in his *Stoichiometry*, 1792-4. His reasoning is obscured by attempts to find mathematical relationships where Nature has not provided any; it was clearly stated in the German translation by E. G. Fischer of Berthollet's *Researches on the Laws of Affinity* (1802). In this a table of equivalent weights of acids and bases appears, part of which is given below.

Bases.			Acids.		
Alumina	-	525	Fluoric	-	427
Ammonia	-	672	Carbonic	-	577
Lime	-	793	Muriatic	-	712
Soda	-	859	Oxalic	-	755
Potash	-	1605	Sulphuric	-	1000
Barvta	-	2222	Nitric	-	1404

"The meaning of this table," said Fischer, "is that, if a substance is taken from one of the two columns, say potash from the first, to which corresponds the number 1605, the numbers in the other column indicate the quantity of each acid necessary to neutralise these 1605 parts of potash. There will in this case be required 712 parts of muriatic [hydrochloric] acid, 577 parts of carbonic acid, etc. If a substance is taken from the second column, the first column is to be used to ascertain how much of an earth or of an alkali is required to neutralise it."

This table of twelve numbers gives by addition in pairs the composition of thirty-six salts. By analysis of six salts, say those corresponding with the horizontal lines, the compositions of the other thirty may be calculated.

Richter's result is a special case of the law of equivalent proportions: *the weights of two (or more) substances which separately react chemically with identical weights of a third are also the weights which react with each other, or are related to them in the ratio of whole numbers, usually small.*

An important case of the law is that which applies to the combination of elements. The equivalent weights of the elements are fundamental values, since the equivalent weights of compounds are formed additively from those of their elements.

In forming a table of equivalents, the equivalent of a standard element must be chosen; Dalton took hydrogen as 1 (since its equivalent is the

smallest of all), Berzelius took oxygen = 100. When hydrogen = 1, the equivalent of oxygen is not quite 8 (see p. 190) ; at present the standard is oxygen = 8, when the accurate value for hydrogen is 1.008.

1.008 parts of hydrogen combine with :	1.008 parts of hydrogen are displaced by :	8 parts of oxygen combine with :
8 or 16 of oxygen	9 of aluminium	35.5 of chlorine
35.5 of chlorine	12 of magnesium	12 of magnesium
80 of bromine	20 of calcium	20 of calcium
127 of iodine	23 of sodium	23 of sodium
16 of sulphur	28 of iron	18.66 or 28 of iron
20 of calcium	32.5 of zinc	31.5 or 63 of copper
23 of sodium	59.5 of tin	29.75 or 59.5 of tin
63 of copper	63 of copper	100 or 200 of mercury
35.5 parts of chlorine combine with :	<i>Weights of metals displacing one another from compounds :</i>	
12 of magnesium	12 of magnesium	
20 of calcium	20 of calcium	
23 of sodium	28 of iron	
32.5 of zinc	31.5 of copper	
18.66 or 28 of iron	32.5 of zinc	
29.75 or 59.5 of tin	59.5 of tin	
31.5 or 63 of copper	100 or 200 of mercury	
100 or 200 of mercury	107.9 of silver	

The figures in this table agree with the law of equivalent proportions and show the weights of various elements which combine together or displace one another from compounds. These are called **combining weights** or **equivalent weights** or (usually) **equivalents**. In some cases an element has more than one equivalent but these are always in a whole number ratio ; in the cases of oxygen, copper, tin and mercury this is 1 : 2 ; in the case of iron it is 2 : 3.

The determination of equivalents.—Equivalents are determined experimentally in various ways.

(1) The weight of an element combining with or displacing 1.008 parts of hydrogen is found. This applies to metals which dissolve in acids or alkalis with evolution of hydrogen, the volume of which is measured.

(2) The weight of a metal displaced from a solution of one of its salts by the equivalent of another metal in class (1) is found. Thus, the equivalent of zinc is found by measurement of the hydrogen evolved by zinc from an acid, and the equivalent of copper is found by weighing the copper displaced by a known weight of zinc from a solution of copper sulphate.

(3) The weight of an element combining with 8.00 parts of oxygen is found ; combination may take place directly, as when magnesium is heated in air or oxygen, or indirectly as when tin or copper is treated with nitric acid, and the product heated to redness. If an oxygen compound is decomposed on heating, *e.g.* mercuric oxide or potassium chlorate, the weight

of oxygen liberated is found, and the equivalent of mercury or of potassium chloride can be calculated.

(4) The equivalent of silver is found by converting a known weight of silver into silver chloride by heating in a current of chlorine, and calculating the weight of silver combining with 35.5 parts of chlorine. A known weight of silver is dissolved in nitric acid and the weight of a chloride of an element, *e.g.* potassium chloride, which just completely precipitates the silver nitrate solution as silver chloride is found. The equivalent of potassium chloride is the amount which just precipitates the equivalent of silver from the silver nitrate solution.

(5) A given weight of one compound, composed of elements of known equivalents may be converted into another compound, containing the element of which the equivalent is desired. Thus, potassium chloride is converted into potassium nitrate by repeated evaporation with nitric acid. From the known equivalent of potassium chloride, the equivalent of potassium nitrate is calculated.

An apparatus for the determination of the equivalent of a metal by method (1) is shown in Fig. 57. A suitable weight of the metal is put into the small tube which is supported in the flask containing the acid or alkali solution by a thread pinched by the rubber stopper. The apparatus is fitted together, the bottle being filled with water. The metal is brought into the liquid by loosening the stopper for a moment, when hydrogen is evolved and displaces water from the bottle into the measuring cylinder when the clip is opened. When action ceases and the flask has cooled to room temperature, the volume of water in the cylinder is read off after equalising the levels. The gas volume is reduced to ml. at S.T.P. and when multiplied by 0.00009 gives the weight of hydrogen displaced by the weight of metal taken. The weight of metal displacing 1.008 gm. of hydrogen is the equivalent. Zinc, magnesium, iron and calcium may be dissolved in cold dilute sulphuric or hydrochloric acid, tin in hot concentrated hydrochloric acid, and aluminium in a mixture of equal volumes of concentrated hydrochloric acid and water or in warm dilute sodium hydroxide solution.

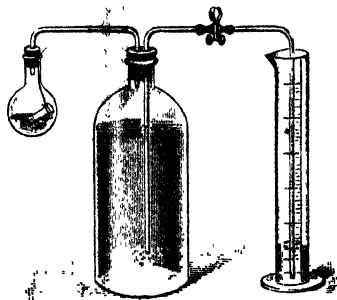


FIG. 57.—Apparatus for determination of equivalents.

Exact determination of equivalents.—The equivalents of some important elements were accurately determined by the Belgian chemist Jean Servais Stas (1813–1891), whose numbers were accepted for a long time as the best values.

Stas began with an analysis of potassium chlorate, which on heating gives off oxygen and leaves potassium chloride. He found that 127.2125 gm. of potassium chlorate gave on heating 77.4023 gm. of potassium chloride, hence the oxygen given off weighed 49.8102 gm. Potassium

chlorate is known to contain 6 equivalents of oxygen, hence the equivalent of potassium chloride, x , is given by :

$$6 \times 8 : x = 49.8102 : 77.4023 ; \therefore x = 74.59.$$

14.427 gm. of potassium chloride gave on precipitation with silver nitrate solution 27.732 gm. of silver chloride, hence the equivalent of silver chloride is given by

$$74.59 : x = 14.427 : 27.732 ; \therefore x = 143.37.$$

101.519 gm. of pure silver when heated in a current of chlorine gave 134.861 gm. of silver chloride, so that the equivalent of silver is given by

$$143.37 : x = 134.861 : 101.519 ; \therefore x = 107.93.$$

Hence the equivalent of chlorine is $143.37 - 107.93 = 35.44$, and the equivalent of potassium is $74.59 - 35.44 = 39.15$.

In 1895 Morley determined the combining ratio of hydrogen and oxygen and found 1 : 7.9395 ; Scott (1893) and Burt and Edgar (1916) found 1 : 7.938. The equivalent of chlorine was determined with reference to hydrogen by Dixon and Edgar (1905) and Edgar (1908) by burning hydrogen and chlorine together, and by Gray and Burt (1909) from the density of hydrogen chloride gas, and the decomposition of the latter by heated aluminium with liberation of hydrogen. The equivalent of chlorine so found, 35.187 ($H = 1$) referred to oxygen = 8.000, is thus

$$35.187 \times 8.000 \div 7.938 = 35.458,$$

which differs from Stas's figure by as much as 1 in 1500.

The modern equivalents of most of the important elements are based on the equivalents of silver, chlorine or bromine. Oxygen appears in few direct ratios and practically no oxides are suitable for exact analysis. The oxides of metals cannot usually be obtained sufficiently pure.* Of the fundamental secondary standards, bromine forms a most unstable oxide, the oxides of chlorine are explosive and difficult to prepare in a state of purity, and pure silver oxide cannot be obtained. On the oxygen standard Stas's value for nitrogen was involved as an intermediate link in the ratio *silver/silver nitrate*.

To find the combining weight of nitrogen, Stas dissolved a known weight of pure silver in nitric acid, evaporated the solution to dryness, and weighed the silver nitrate. He found the ratio *silver/silver nitrate* = 100 : 157.484, and from the equivalent 107.93 of silver he calculated the combining weight of nitrogen as 14.05. Gas densities and analyses of gaseous oxides or nitrogen, however, showed that the value was lower, viz. 14.008. T. W. Richards found that Stas's silver, distilled in a lime retort with the oxyhydrogen blowpipe, contained a little oxygen. Richards prepared his silver by reducing recrystallised silver nitrate and fused it in hydrogen.

* It is commonly stated that "hydrogen combines with only a few elements" and that "oxygen compounds are more suitable for analysis than hydrogen compounds". Neither of these statements is correct in the light of modern knowledge.

Richards profited by the improved laboratory facilities which had become available since Stas's time, particularly in purifying materials, especially the silver; he used platinum or quartz vessels, electric heating, and a centrifuge for separating solids from liquids. Richards also invented two important new devices, the *bottling apparatus* and the *nephelometer*.

(1) The *bottling apparatus* (Fig. 58) is a hard glass or quartz tube *A* fitted by a ground joint to a soft glass tube *B* with a pocket *C*. A platinum boat

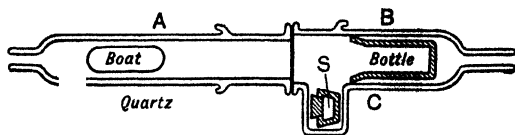


FIG. 58.—Bottling apparatus.

containing the substance was put into *A*, the weighing bottle into *B* and the stopper *S* in *C*. The boat was heated in a current of a gas. After cooling, the gas was displaced by dry air and the boat pushed into the weighing bottle, after which the stopper was similarly inserted. The bottle was then transferred to the balance. Hönigschmid's apparatus is similar, but the boat and stopper are moved by the action of a magnet on a bulb containing iron.

(2) The *nephelometer* (Greek *nephele*, a cloud) determined traces of sparingly soluble substances such as silver chloride dissolved in the washings. In this case excess of silver nitrate was added, when (owing to the common ion effect, p. 312) a small amount of silver chloride was precipitated from the solution and an opalescence developed, which was compared with a standard in the nephelometer. This consists (Fig. 59) of two test-tubes containing the liquids and inclined in an inverted V, partly screened from bright light by two shutters, one moving over a scale. If the shade over the standard covered half the tube when the same appearance was seen from above, viewed through two flat prisms, then a new standard about half as concentrated was put in, and a new comparison made. In this way the amount of suspended substance was accurately determined and a suitable correction applied.

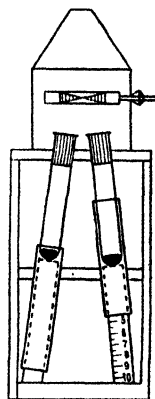


FIG. 59.—Nephelometer.

Richards and Forbes (1905) redetermined the ratio *silver/silver nitrate* by Stas's method, finding 100 : 157.479. With various *assumed* values for silver the corresponding combining weights of nitrogen were calculated as :

Silver	-	-	107.93	107.89	107.88
Nitrogen	-	-	14.037	14.014	14.008

Since accurate physico-chemical methods (limiting densities, etc.) had given

the value nitrogen = 14.008, silver must be taken as 107.88 to agree with this.

Hönigschmid (1927) found the same value for the ratio *silver/silver nitrate* by the dry reduction of silver nitrate to metallic silver. Hönigschmid and Sachtleben (1929) first referred silver independently to oxygen by (i) converting a known weight of pure barium perchlorate into chloride by heating in hydrogen chloride gas, thus finding the ratio *barium chloride/oxygen* (the solids were weighed in vacuum to avoid errors due to adsorbed gas), (ii) precipitating the barium chloride as silver chloride and so finding the ratio *barium chloride/silver chloride*. From the two ratios they calculated the equivalent of silver as 107.880. This value is now accurately known, and since in the majority of cases equivalents are determined relative to silver as a secondary standard, this is very important.

THE ATOMIC THEORY

The law of conservation of mass, the law of constant proportions, the law of multiple proportions, and the law of equivalents were first explained on the basis of the atomic theory by John Dalton in 1803.* The atomic theory supposes matter to be composed of very small indivisible particles called atoms, from the Greek meaning "something which cannot be cut". Leukippos and Demokritos, the Greek philosophers, about 450 B.C. made use of the atomic theory in a rudimentary and qualitative form.

Dalton's atomic theory asserts that :

(1) The chemical elements are composed of very minute particles of matter called atoms, which remain undivided in all chemical changes.

The atom is the smallest mass of an element which can take part in a chemical change.

(2) Each kind of atom has a definite weight. Different elements have atoms differing in weight.

(3) Atoms combine in simple numerical ratios, e.g. 1 atom *A* + 1 atom *B*; 1 atom *A* + 2 atoms *B*; 2 atoms *A* + 1 atom *B*; 2 atoms *A* + 3 atoms *B*, etc.

These simple assumptions will explain the laws of chemical combination.

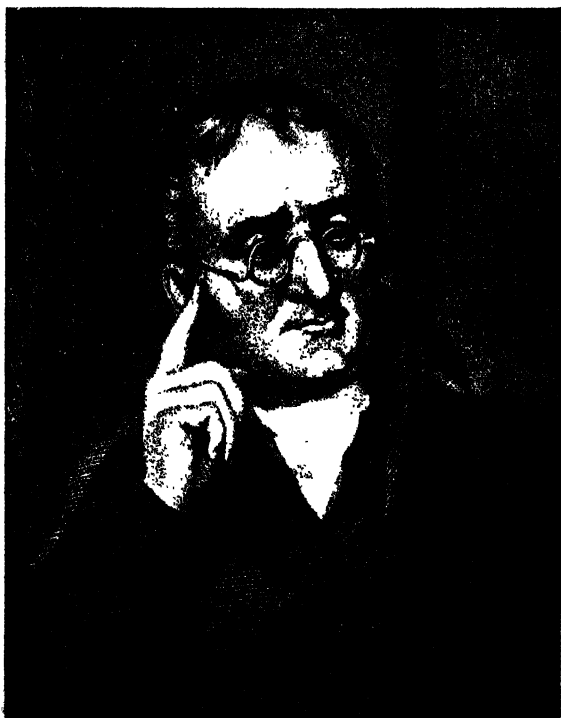
In the first place, atoms are indestructible in chemical changes, so that we see the necessity of the *law of conservation of mass*.

In the modern atomic theory (see Chapter XXIII) an atom is assumed to contain a very small positively charged nucleus, surrounded by negatively

* See *Alembic Club Reprint No. 2*. The story that Dalton was led to the atomic theory from results of his analyses of methane and ethylene, giving a multiple ratio of 1 : 2 for carbon combined with identical weights of hydrogen, has long been known to be incorrect. The true origin of the theory is sketched in Partington's *A Short History of Chemistry*, p. 174.

charged electrons so that the atom as a whole is neutral. The atomic nuclei, which contain all but a small part of the mass of the atom, enter and leave chemical changes unaffected, but some of the outer electrons are removed or redistributed. This part of Dalton's theory is, therefore, essentially retained.

The smallest particle of a compound, called a "compound atom" by Dalton, is now called a molecule. He assumed that the molecules of



JOHN DALTON (1766-1844).

a compound are all alike, formed of fixed numbers of atoms of its elements, and that all atoms of the same element are identical in all respects, particularly in weight or mass. This explains the *law of constant proportions*.

Dalton's assumption has been modified by the discovery of isotopes, and can no longer be maintained. One element, *e.g.* chlorine, may have atoms differing in mass, and the atoms of such an element are not necessarily all the same, since the ordinary element may be a mixture of isotopes. It is not the mass of its atom, the atomic weight, which characterises an element; modern theory teaches that this part is played by the positive charge on the nucleus of the atom, the so-called atomic number (p. 393). All isotopes

have the same atomic number, although they may have different atomic masses. The "element lead" is any one of the several isotopes of lead, or mixtures of any or all of them in any proportions.

If two elements combine in more than one ratio, the molecules of the compounds must contain whole numbers of atoms of the elements: m atoms $A + n$ atoms B , and x atoms $A + y$ atoms B . The numbers of atoms of B combined with one atom of A are n/m and y/x , in the ratio nx/my , i.e. in the ratio of whole numbers; hence the weights of B combining with identical weights of A are in the ratio of whole numbers. This is the Law of Multiple Proportions.

Compounds of the elements A and C must be formed according to the scheme: m atoms $A + n$ atoms C . Compounds of the elements B and C must be composed of: x atoms $B + y$ atoms C . Compounds of the elements A and B must contain: p atoms $A + q$ atoms B . But x , y , m , n , p , q are whole numbers, usually small. Hence p , q are either the same as m , x , or whole multiples of them, usually small. This is the Law of Equivalent Proportions.

Atomic weights.—The absolute weights of atoms are very small and Dalton attempted to find only the relative weights, taking the weight of the lightest atom, that of hydrogen, as unity. The atomic weight of an element was then the number giving the ratio of the weight of an atom of that element to the weight of an atom of hydrogen. Dalton's original atomic theory provided no means of determining even the relative weights of atoms. Although 8 parts of oxygen combine with 1 part of hydrogen, we do not know how many atoms of each element the molecule of water contains. If it contains 1 atom of each element (as Dalton supposed), the atomic weight of oxygen is 8, but if it contains 2 atoms of hydrogen to 1 atom of oxygen, as the volume ratio of the combining gases would suggest, the atomic weight of oxygen is $2 \times 8 = 16$.

The existence of three isotopes of masses 16, 17, and 18, in ordinary oxygen makes the "chemical" atomic weights, determined with respect to $O = 16.000$, really about 2 parts in 10,000 smaller than those determined (say by the mass spectrograph) by "physical" methods, which are referred to the isotope $^{16}O = 16.000$ (Aston, *J. Chem. Soc.*, 1932, p. 2890).

If the absolute weight (or mass) of any one atom is determined, those of all the others are found by simple multiplication of this by the ratios of the atomic weights. In recent years the mass of the hydrogen atom has been found by several different methods to be 1.66×10^{-24} gm. Thus, 1 ml. of hydrogen, at S.T.P., weighing 0.00009 gm., contains 5.4×10^{19} atoms. The weight of the uranium atom (atomic weight 236), is $236 \times 1.66 \times 10^{-24} = 3.92 \times 10^{-22}$ gm.

Chemical nomenclature and notation.—The method of naming chemical substances is chemical nomenclature; their representation by symbols is chemical notation.

The nomenclature of the alchemists was empirical. The same substance had a variety of names, depending on its mode of preparation, and names

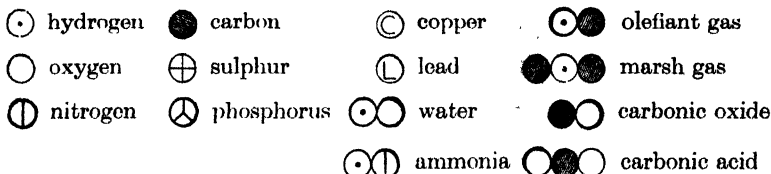
were often based on accidental resemblances. Thus *butter of antimony* was classed with ordinary butter, and *oil of vitriol* (sulphuric acid) with olive oil.

A scientific nomenclature began with Macquer and Baumé, who classed together the glassy, crystalline substances: *white vitriol* (zinc sulphate), *green vitriol* (ferrous sulphate), and *blue vitriol* (copper sulphate). Bergman's system of nomenclature (1782) indicated the basic and acidic constituents of salts. *E.g.* salts of potash or the vegetable alkali, were named *vegetabile vitriolatum* (potassium sulphate), *vegetabile nitratum* (potassium nitrate).

The modern chemical nomenclature had its origin in a treatise (*Méthode d'une Nomenclature chimique*, 1787) drawn up by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, in order to make the antiphlogistic doctrines less dependent on names which had arisen during the phlogistic period.

Some elements (copper, gold, tin, sulphur) retain their old names; newly discovered metals have names ending in *-um* and non metals in *-on* (except deuterium).

Dalton used circular symbols for atoms:



The present chemical notation is an extension by Berzelius (1813) of a system used by Thomson (1802); it replaced Dalton's symbols by the initial letter, or the initial and one other letter, of the Latinised name of the element. A list of symbols is given inside the front cover. The symbol has a quantitative significance, and represents one atom or one atomic weight of the element. O represents 16 parts by weight of oxygen; Cl 35.5 parts by weight of chlorine, etc. This is the most important feature of the system of chemical notation.

The names of compounds indicate their composition. In names of compounds of two elements, the name of the more electropositive (p. 374) element comes first, followed by the name of the other element suitably contracted and with the termination *-ide*. The order in which the elements are taken in forming the names should be as follows:

Metals.

Carbon.

Nitrogen, phosphorus, arsenic.

Hydrogen.

Sulphur, selenium, tellurium.

Halogens (fluorine, chlorine, bromine, iodine).

Oxygen.

The formulae of compounds are made up by writing the symbols of the elements together, with a small numerical suffix to indicate how many atoms of each element are present in a molecule of compound, unity being always understood.

Since two elements may combine in more than one ratio, this is represented by suffixes added to the Latin names, or by prefixes :

Cu ₂ O, cuprous oxide	}	Suffixes.	SO ₂ , sulphur dioxide	}	Prefixes.
CuO, cupric oxide			SO ₃ , sulphur trioxide		

The suffix *-ous* denotes the *lower*, and *-ic* the *higher*, proportion of oxygen, chlorine, etc. In a series of oxides, the one containing the *highest* proportion of oxygen is sometimes called a peroxide, but it has been proposed to restrict this name to a special class of oxides, giving hydrogen peroxide (H₂O₂) with acids, such as Na₂O₂, BaO₂. The name peroxide is used rather loosely.

A chemical change is represented by an equation, which indicates how many molecules of the initial substances interact to produce the specified number of molecules of the products. The numbers of atoms of every element must be the same on both sides of the equation, that is, the equation must be *balanced*.

Valency.—The ratio of the atomic weight to the equivalent is equal to the valency of an element.

$$\text{Valency} = \frac{\text{Atomic Weight}}{\text{Equivalent}}$$

The valency of oxygen is $16/8 = 2$; that of copper is $63/31.5 = 2$ in the *cupric* compounds, and $63/63 = 1$ in the *cuprous* compounds.

The valency of hydrogen is 1, since the atomic weight is equal to the equivalent. If *E* is the equivalent, *A* the atomic weight, and *n* the valency of an element, $A = nE$. Since 1 atom of hydrogen combines with a weight *E*, it follows that *n* atoms of hydrogen will combine with a weight *A*, hence this number *n* is equal to the valency.

Hydrogen compounds are known in which one atom of an element is combined with one, two, three, or four atoms of hydrogen :

HCl	H ₂ O	H ₃ N	H ₄ C
Hydrochloric acid	Water.	Ammonia	Methane.

The atoms of chlorine, oxygen, nitrogen, and carbon can unite with one, two, three, and four atoms of hydrogen, respectively. None of these compounds of hydrogen contains more than one atom of an element combined with one atom of hydrogen,* and the latter is taken as the standard of combining capacity or valency. *The valency of an element is measured by the number of hydrogen atoms which unite with one atom of that element.* The elements chlorine, oxygen, nitrogen, and carbon are univalent, bivalent, trivalent, and quadrivalent respectively.†

* The only case in which 1 atom of hydrogen combines with more than 1 atom of another element is hydrazoic acid HN₃ in which the azide group -N₃ is univalent.

† The hybrid names *mono-*, *di-*, *tri-*, *tetra-* and *penta-*valent are often used instead of the more correct *uni-*, *bi-*, *ter-*, *quadri-* and *quinque-*valent. Elements with valencies of 6, 7 and 8 are called *sextivalent*, *septavalent*, and *octovalent*, respectively. In this book the convenient abbreviations 2-, 3-, 4-, 5-, 6-, 7- and 8-valent will be used.

Since chlorine is univalent it may be used instead of hydrogen in determining the valencies of elements, which are the same as those referred to hydrogen, but quinquivalent elements are now included :

Cl_2O Chlorine monoxide.	Cl_3N Nitrogen trichloride	Cl_4C Carbon tetrachloride.	Cl_5P Phosphorus pentachloride.
------------------------------------------------	--------------------------------------------------	---------------------------------------------------	-------------------------------------------------------

Oxygen is bivalent and if it combines with one atom of another element the latter (*e.g.* calcium in calcium oxide CaO) is also bivalent and will combine with two atoms of hydrogen (CaH_2) or chlorine (CaCl_2). In oxygen compounds the additional valencies 6, 7 and 8 appear, the highest valency known being 8 :

Na_2O Sodium monoxide.	CaO Calcium oxide.	Al_2O_3 Aluminium oxide.	CO_2 Carbon dioxide.
* P_2O_5 Phosphorus pentoxide	SO_3 Sulphur trioxide	Cl_2O_7 Chlorine heptoxide.	OsO_4 Osmium tetroxide.

Sulphur is 6-valent, chlorine is 7-valent and osmium is 8-valent in their highest oxides.

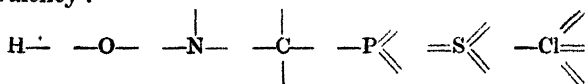
The valency of an element is often represented by a roman numeral :



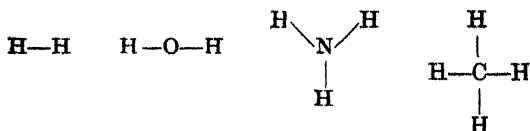
An element may have a *variable* valency either in its compounds with the *same* element, or in its compounds with *different* elements :

PCl_3 (3)	SO_2 (4)	PH_3 (3)	SH_2 (2)
PCl_5 (5)	SO_3 (6)	P_2O_5 (5)	SF_6 (6)

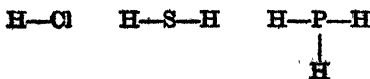
Structural formulae.—We may form a picture of the combination of atoms by assuming that each atom has one or more bonds, shown by straight lines drawn from the symbol of the atom, each bond representing one valency :



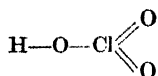
In chemical combination these bonds unite in pairs. In writing the formulae of the compounds, the pairs of bonds are contracted to single bonds :



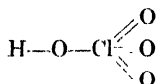
Higher valencies of elements.—The elements chlorine, sulphur and phosphorus show valencies of one, two and three in simple compounds with hydrogen :



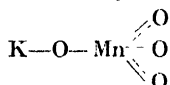
In the oxy-acids of these elements the atoms show higher valencies. The formula of chloric acid, for example is written :



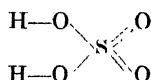
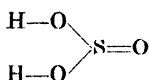
in which chlorine is 5-valent, and the formula of perchloric acid is :



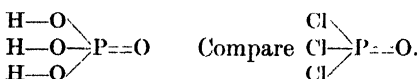
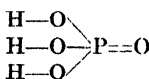
in which chlorine is 7-valent. A similar formula is assumed for potassium permanganate,* in which manganese, which is bivalent in simple compounds such as MnCl_2 and MnSO_4 , is now 7-valent :



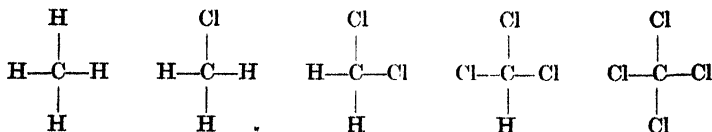
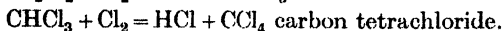
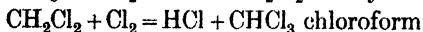
The formulae of sulphur dioxide and trioxide may be written so as to make sulphur 4-valent and 6-valent, respectively, and sulphur may be supposed to have these valencies in sulphurous and sulphuric acids :



In phosphoric acid the phosphorus may be regarded as 5-valent :



Saturated and unsaturated compounds.—Since in methane CH_4 all the valencies of the carbon are united with hydrogen, chlorine can react only by turning out the hydrogen (as hydrochloric acid) and taking its place—a so-called substitution reaction (p. 607). Four compounds are produced :



In some cases *two* or more valencies of an atom of an element can

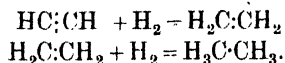
* The salt actually consists of two separate ions, K^+ and MnO_4^- , but the valency of Mn in the ion is 7.

unite with a corresponding number of valencies of an atom of the *same* element :

- | | | |
|--------------|----------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| 1. Ethane | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | single bond, or linkage, between carbon atoms. |
| 2. Ethylene | $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | double bond, or linkage, between carbon atoms. |
| 3. Acetylene | $\text{H}-\text{C}\equiv\text{C}-\text{H}$ | triple bond, or linkage, between carbon atoms. |

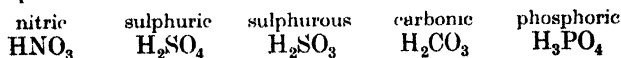
Such bonds are often represented by dots $\text{H}_3\text{C}\cdot\text{CH}_3$, $\text{H}_2\text{C}:\text{CH}_2$ and $\text{HC}:\text{CH}$.

Molecules of compounds with multiple bonds are *unsaturated*, *i.e.* can add on other atoms to form saturated compounds which react only by substitution :

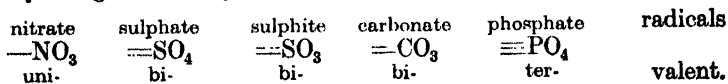


Valencies of radicals.—The idea of valency may be extended to radicals. Molecules such as O_2 , H_2O and CO_2 , in which the valencies of the elements are balanced, are called *saturated*. Radicals are parts of saturated molecules; they possess valency, and do not ordinarily occur in the free state. Water may be regarded as a compound of the hydrogen atom with the hydroxyl radical, $\text{H}-\text{OH}$, hence the radical OH is univalent. Sodium in sodium hydroxide, $\text{Na}-\text{OH}$, is also univalent.

An inspection of the formulae of the common acids :



shows that the valencies of the acid radicals are as shown below, each valency being denoted by a stroke :



Valencies of the elements.—The elements may be classified into groups according to their valencies. The inert gases (helium, argon, etc.) and the radioactive emanations do not combine with any other elements and are *zero-valent*. The other elements have the following valencies. The same element may appear in more than one group, since its valency may vary.

I. Univalent elements : hydrogen, halogens, alkali metals, copper in cuprous compounds (CuCl , Cu_2O), silver, gold in AuCl and Au_2O .

II. Bivalent elements : oxygen, sulphur in H_2S , and a large number of metals, e.g. alkalino-earth metals (Ca, Sr, Ba), magnesium, zinc, cadmium, mercury, tin in stannous compounds ($\text{SnCl}_2, \text{SnO}$), lead in plumbous compounds ($\text{PbCl}_2, \text{PbO}$), iron in ferrous compounds ($\text{FeCl}_2, \text{FeO}$), manganese in manganous compounds ($\text{MnCl}_2, \text{MnO}$), chromium in chromous compounds ($\text{CrCl}_2, \text{CrO}$), etc.

III. Trivalent elements : boron, nitrogen ($\text{NH}_3, \text{NCl}_3$), phosphorus ($\text{PH}_3, \text{PCl}_3$), arsenic ($\text{AsH}_3, \text{AsCl}_3, \text{As}_2\text{O}_3$), antimony ($\text{SbH}_3, \text{SbCl}_3, \text{Sb}_2\text{O}_3$), bismuth ($\text{BiCl}_3, \text{Bi}_2\text{O}_3$), aluminium, iron in ferric compounds ($\text{FeCl}_3, \text{Fe}_2\text{O}_3$), chromium in chromic compounds ($\text{CrCl}_3, \text{Cr}_2\text{O}_3$), gold in AuCl_3 .

IV. Quadrivalent elements : carbon, silicon, lead in plumbic compounds ($\text{PbCl}_4, \text{PbO}_2$), tin in stannic compounds ($\text{SnCl}_4, \text{SnO}_2$).

V. Quinquevalent elements : phosphorus ($\text{PCl}_5, \text{P}_2\text{O}_5$), arsenic (As_2O_5), antimony ($\text{SbCl}_5, \text{Sb}_2\text{O}_5$), chlorine in chloric acid HClO_3 and chlorates, iodine in I_2O_5 , iodic acid HIO_3 and iodates.

VI. Sexivalent elements : sulphur in $\text{SF}_6, \text{SO}_3, \text{H}_2\text{SO}_4$ and sulphates; chromium in CrO_3 and chromates, manganese in manganates K_2MnO_4 .

VII. Septavalent elements : chlorine in Cl_2O_7 , perchloric acid HClO_4 and perchlorates; iodine in periodic acid HIO_4 and periodates; manganese in Mn_2O_7 and permanganates KMnO_4 .

VIII. Octovalent elements : osmium in OsF_8 and OsO_4 , ruthenium in RuO_4 .

The properties of an element differ in the compounds in which it has different valencies. Silver and cuprous chlorides, AgCl and CuCl , are white insoluble solids; cupric and mercuric chlorides, CuCl_2 and HgCl_2 , are soluble. Bivalent lead and tin compounds are similar, as are quadrivalent lead and tin compounds, but the compounds in different groups, e.g. SnCl_2 and SnCl_4 , are quite different in properties.

CHAPTER IX

AVOGADRO'S HYPOTHESIS AND MOLECULAR WEIGHTS

The law of gaseous volumes.—The combining volumes of hydrogen and oxygen were found by Cavendish to be very nearly 2 : 1. Alexander von Humboldt and Joseph Louis Gay-Lussac in 1805 confirmed this result. Gay-Lussac was impressed by the simple whole-number ratio, and extended his researches to other chemical reactions between gases. In 1808 he announced the law of gaseous volumes: *when gases take part in chemical changes the volumes of the reacting gases, and those of the products if gaseous, are in the ratio of small whole numbers.**

The same conditions of temperature and pressure are assumed.

1 volume of oxygen combines with 2 volumes of hydrogen to give 2 volumes of steam.

2 volumes of carbonic oxide combine with 1 volume of oxygen to give 2 volumes of carbonic acid.

2 volumes of nitrogen combine with 1 volume of oxygen to give 2 volumes of nitrous oxide.

1 volume of nitrogen combines with 1 volume of oxygen to give 2 volumes of nitric oxide.

1 volume of nitrogen combines with 2 volumes of oxygen to give 2 volumes of nitrogen dioxide.

1 volume of nitrogen combines with 3 volumes of hydrogen to give 2 volumes of ammonia.

1 volume of chlorine combines with 1 volume of carbon monoxide to give 1 volume of carbonyl chloride.

Later experiments (p. 188) showed that the law is not quite exact. Burt and Edgar found the combining volumes of hydrogen and oxygen to be 2.00288 : 1; Gray and Burt from 2 volumes of hydrochloric acid gas obtained 1.0079 volumes of hydrogen; Guye and Pintza showed that 1 volume of nitrogen combines with 3.00172 volumes of hydrogen to form ammonia. All these numbers refer to S.T.P. The slight differences from whole numbers appear to be due to the different compressibilities of the gases, *i.e.* the deviations from Boyle's law.

* Gay-Lussac's own words (published in 1809) are: "ces substances se combinent entre elles dans des rapports très-simples, et la contraction de volume qu'elles éprouvent par la combinaison suit aussi une loi régulière".

Dalton seems to have assumed that the results of Gay-Lussac required that equal volumes of elementary gases contain equal numbers of atoms and he had previously rejected this assumption. In the first place, Dalton's own (inexact) measurements of combining volumes did not confirm Gay-Lussac's law: he found that 1.97 volumes of hydrogen combine with 1 volume of oxygen. In the second place, he pointed out that the density of a gas is not the same thing as the weight of its ultimate particle: steam is lighter than oxygen, whereas the ultimate particle of steam must be heavier than that of oxygen, since it contains the latter.

Berzelius assumed that equal volumes of elementary gases contain equal numbers of *atoms*. Let us see how this works out if we assume that the compound gas also contains the same number of particles in the same volume as the elementary gases. Let us represent the volumes by squares, which we may regard as sections of cubes containing equal volumes of gases. Take the case of hydrogen and chlorine and represent a hydrogen atom by ● and a chlorine atom by ○.

We see from Fig. 60 that we cannot make the volumes right, because to do this hydrogen chloride would have to contain only half as many particles as an equal volume of hydrogen or chlorine. Dalton pointed

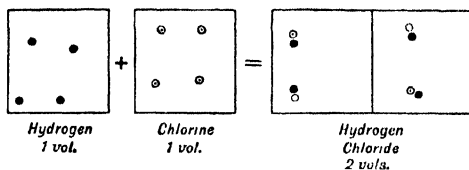


FIG. 60.—Combination of hydrogen and chlorine according to Berzelius.

out this difficulty. It was overcome by the Italian scientist Amedeo Avogadro (1776–1856) in 1811.

Avogadro's hypothesis.—Avogadro began by assuming that :*

Equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain identical numbers of molecules.

A molecule is the smallest mass of a substance capable of existing in the free state.

Avogadro showed that it is necessary to assume that the particles of elementary gases are not atoms but are divisible molecules.

Let us assume that the molecules of hydrogen and chlorine each contain *two* atoms and that they are divided when the gases react. Then

* Avogadro's own words are: "le nombre des molécules dans les gaz quelques est toujours le même à volume égal . . . les rapports des masses des molécules sont alors les mêmes que ceux des densités des différents gaz, à pression et température égales". The memoir is in French.

the volume relations will come out correctly, as we see from Fig. 61, and the formula of hydrogen chloride is found to be HCl :

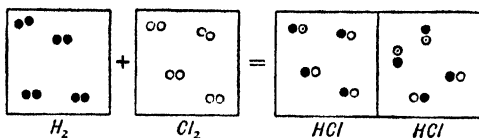
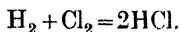


FIG. 61.—Combination of hydrogen and chlorine according to Avogadro.

In ordinary symbols :



Suppose one volume of hydrogen contains 100 molecules ; it reacts with an equal volume of chlorine, which Avogadro's hypothesis shows must also contain 100 molecules, to form *two* volumes of hydrogen chloride, which must contain 200 molecules. Each of these 200 molecules must contain at least one atom of hydrogen and one of chlorine, hence the 100 molecules of hydrogen and the 100 of chlorine must have been divided into two parts, which we can suppose are the atoms.

Another example is the formation of steam from hydrogen and oxygen, and the formula of steam is seen to be H_2O :

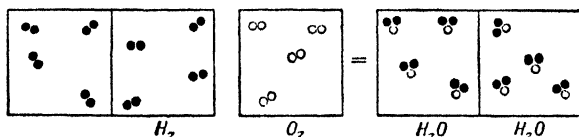


FIG. 62.—Combination of Hydrogen and Oxygen.

These formulae depend on the assumption that the molecules of hydrogen, oxygen and chlorine contain *two* atoms. This is the simplest assumption which explains the results, and we assume that it is the correct one.

There is some physical evidence, *e.g.* the value 1.4 for the specific heat ratio c_p/c_v (p. 126), that the molecules of hydrogen, oxygen, nitrogen and hydrogen chloride contain two atoms, or are *diatomic*. The number of atoms in a molecule of an element is called the *atomicity*.

Molecules of elements in the gaseous state may contain from one to eight atoms :

Monatomic : Na, K, Zn, Cd, Hg, He, A, Ne, Kr, Xe, Rn, I, Cl, Bi.

Diatomic : H_2 , O_2 , N_2 , Cl_2 , Br_2 , I_2 , F_2 , S_2 , Se_2 , Te_2 , As_2 , Sb_2 , Bi_2 .

Triatomic : O_3 .

Tetratomic : P_4 , As_4 .

Hexatomic : S_8 (?).

Octatomic : S_8 .

The absence of the types X_5 and X_7 is noteworthy.

Maxwell defined a molecule of a gas as *that small portion of matter which moves about as a whole so that its parts, if it has any, do not part company during the motion of agitation of the gas.* The molecule of a substance may be different under different conditions. The molecule of iodine vapour at temperatures below 700° consists of two atoms, I_2 . At higher temperatures an increasing number of I_2 molecules decompose into atoms, $I_2 = 2I$, and in this case the atom is identical with the molecule. In many solid salts, the crystal is a regular aggregate of electrically charged atoms or ions; in common salt, for example, the molecule $NaCl$ is not present as an individual, but only charged sodium and chlorine ions, Na^+ and Cl^- , arranged in a cubical packing. In solution in water, common salt is present as sodium and chlorine ions, not as $NaCl$ molecules. In the vapour the molecules $NaCl$ are present. In liquid water there appear to be molecules more complex than H_2O , which is present in steam, *i.e.* $(H_2O)_n$ molecules. The definition of the molecule in any particular state follows from the determination of the molecular weight and a particular material may contain several kinds of molecules, *e.g.* I_2 and I in iodine vapour.

Molecular weight and density.—It follows from Avogadro's hypothesis (and was stated by him) that *the weights of equal volumes of gases or vapours at the same temperature and pressure are in the ratio of the molecular weights.*

The relative density (p. 49) of a gas (or vapour) is the ratio :

$$\frac{\text{weight of a given volume of the gas or vapour}}{\text{weight of an equal volume of hydrogen}}$$

at the same temperature and pressure.

Avogadro's hypothesis shows that the relative density is also equal to the ratio :

$$\frac{\text{weight of one molecule of the gas or vapour}}{\text{weight of one molecule of hydrogen}}$$

since equal volumes contain identical numbers of molecules.

If the atomic weight of hydrogen is taken as 1 the molecular weight is 2, since it has been shown that the hydrogen molecule contains 2 atoms; hence the relative density of a gas is equal to :

$$\frac{\text{weight of one molecule (molecular weight)}}{2}$$

so that : molecular weight = relative density \times 2.

Actually, on the atomic weight standard oxygen = 16, the atomic weight of hydrogen is 1.008 and its molecular weight is 2.016 instead of 2.

Avogadro's hypothesis shows that a gram molecular weight (or mol) of any gas at S.T.P. occupies the same volume. This is called the **gram molecular volume, or molar volume.**

Let M = molecular weight in grams of a gas, and D = normal density (weight of one litre at S.T.P.). Then :

$$\frac{M}{D} = \text{vol. of 1 mol in litres at S.T.P.} = V_m.$$

For oxygen the molecule has been shown to contain two atoms each of weight 16; $\therefore M = 32$. It is found that $D = 1.429$ gm./lit., hence $V_m = 32/1.429 = 22.4$ litres. Avogadro's hypothesis shows that V_m is the same for all gases, hence

$$M = 22.4D.$$

The relative density is equal to the normal density divided by the normal density of hydrogen, viz. $D/0.09$, hence the normal density of a gas is the relative density multiplied by 0.09. Thus :

molecular weight = (rel. dens. \times 0.09) \times 22.4 = rel. dens. \times 2.016, as before.

Relative densities of gases were formerly referred to air = 1 as standard. The relative density of air = $1.2927 \div 0.08987 = 14.38$, hence the relative density referred to air = 1 is converted to that referred to hydrogen = 1 by multiplication by 14.38. The molecular weight ($O = 16$) is found by multiplying the density relative to air = 1 by 29.00, i.e. $14.38 \times 1.008 \times 2$.

Limiting densities.—The ratio of the normal densities of two gases does not give an exact ratio of the molecular weights. For, even if equal volumes contain equal numbers of molecules at one particular pressure, they would, on account of the different compressibilities of the different gases, not remain exactly equal at another pressure. The numbers of molecules in these unequal volumes would, however, still be equal.

The unequal compressibilities of gases, which result from the deviations from Boyle's law, become less as the pressure decreases, and appear to vanish at very small pressures. It may be assumed that the ratio of the densities at very low pressure, or the ratio of the limiting densities ($p \rightarrow 0$), will give the exact ratio of the molecular weights (D. Berthelot, 1899).

If W gm. of gas at 0° occupy v litres under a pressure p atm., the quotient W/pv is the density per unit pressure. Boyle's law makes this the same at all pressures, since $pv = \text{const.}$ Owing to deviations from Boyle's law, the quotient depends on the pressure. If $p = 1$, we have the normal density; if $p \rightarrow 0$ the quotient approaches the value for an ideal gas, which is the limiting density. The ratio of the limiting densities is the ratio of the molecular weights :

$$M_a : M_b = \frac{W_a}{(p_0 v_0)_a} : \frac{W_b}{(p_0 v_0)_b},$$

where $p_0 v_0$ is the limiting value of pv as $p \rightarrow 0$.

D , the normal density, is $W/p_1 v_1$, where $p_1 v_1$ is the value of pv for $p = 1$,

$$\therefore \text{limiting density} = \text{normal density} \times \left(\frac{p_1 v_1}{p_0 v_0} \right). \quad \dots\dots\dots (1)$$

The ratio p_1v_1/p_0v_0 may be determined for any arbitrary mass of gas by two methods :

(i) For gases which deviate only slightly from Boyle's law between zero pressure and 1 atm., $(p_0v_0 - pv)/pv$, the relative deviation from Boyle's law, may be assumed proportional to the pressure :

$$(p_0v_0 - pv)/p \sim pv = \text{const.} = \lambda. \quad \dots\dots\dots(2)$$

The compressibility coefficient λ may be found from two measurements of pv between 1 atm. and zero pressure.

If $p = 1 \text{ atm.} = p_1$, $v = v_1$, then :

$$p_0v_0 - p_1v_1 = \lambda p_1v_1$$

$$\therefore p_1v_1/p_0v_0 = 1/(1 + \lambda)$$

$$\therefore \text{from (1)} \quad \text{limiting density} = \frac{\text{normal density}}{1 + \lambda}. \quad \dots\dots\dots(3)$$

(ii) From several measurements of pv a curve can be drawn in which pv is plotted against p . Extrapolation to $p = 0$ gives the value of p_0v_0 , and the limiting density is then found by multiplying the normal density by (p_1v_1/p_0v_0) .

EXAMPLE 1.—The atomic weight of hydrogen from the relative density.

	Normal Density.	Compressibility = λ .
Hydrogen	0.089873	- 0.00054
Oxygen	1.42900	+ 0.000964

$$\text{Limiting density of hydrogen} = 0.089873 \times \frac{1}{1 - 0.00054} = 0.089922 \text{ gm./lit.}$$

$$\text{Limiting density of oxygen} = 1.42900 \times \frac{1}{1 + 0.000964} = 1.42762 \text{ gm./lit.}$$

The ratio of the limiting densities is equal to the ratio of the molecular (or in this case the atomic) weights, hence :

$$\text{atomic weight of hydrogen} = \frac{1}{2} \times 0.089922 \times 32/1.42762 = 1.0078.$$

EXAMPLE 2.—The atomic weight of chlorine from the density of hydrogen chloride (Gray and Burt).

	Normal density	p_1v_1	p_0v_0
Hydrogen chloride	1.63915	54803	55213 (extrapolated).
Limiting density of HCl		1.63915×54803	55213
Molecular weight of HCl(H = 1)		$2 \times 1.62698/0.089922$	$= 36.186$.
At. weight of Cl (H = 1)		$= 36.186 - 1$	$= 35.186$.

By heating aluminium in 2 volumes of hydrogen chloride, measured at S.T.P., 1.00790 volumes of hydrogen were obtained. The molecular weight of HCl (H = 1) is therefore :

$$\frac{1.63915}{0.089873} \times \frac{2}{1.00790} = 36.191,$$

agreeing to about 1 part in 10,000 with the value from the limiting density.

The method of limiting densities gives results at least as accurate as those found by chemical methods, and in some cases more accurate values.

The value of the molar volume of an *ideal* gas is given by the limiting density of oxygen as $32/1.42762 - 22.415$ litres per mol.

The microbalance.—Some very accurate determinations of molecular weights of gases have been made with the microbalance, invented by Nernst, and used by R. W. Gray and Ramsay in 1910 for the determination of the density of radium emanation (in which a balance with a sensibility of $1/500,000$ mg., dealing with a volume of 0.1 cu. mm., weighing less than 0.001 mg., was used). It has since been improved and a modern form is shown diagrammatically in Fig. 63.

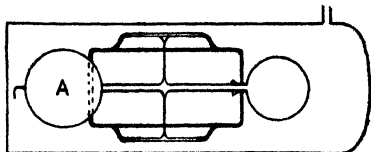


FIG. 63.—Microbalance (plan).

The beam, suspension fibres and parts of the frame were of fused quartz, the bulbs and most of the frame (shown thickened) of Pyrex glass. The bent pointer was attached to the buoyancy bulb *A* and the reading microscope was end-on. The whole was enclosed in a glass cylinder containing the gas, with a plate-glass window at one end and a capillary connection to the pressure system. The adjustment in air was at rather less than 1 atm. pressure and the period of oscillation was 10 sec. Pressure differences of 0.005 mm. were indicated.

The beam is balanced at zero when the gas density in the case exerts a buoyancy effect on the bulb which compensates its net weight. The pressures p_I and p_{II} at which two gases have equal densities are measured.

The balancing pressure ratio $p_I/p_{II} = r$ is extrapolated to the limiting value r_0 for $p_I = p_{II} = 0$, when :

$$M_{II}/M_I = r_0.$$

This microbalance method has been used to determine the atomic weight of carbon from the density of carbon monoxide (Woodhead and R. Whytlaw-Gray, 1933). Corrections were applied for the shrinkage of the buoyancy bulb caused by change of gas pressure outside, and for the shift in the centre of gravity of the bulb due to this shrinkage.

The microbalance method has several advantages over the globe method (p. 50) for the determination of gas densities : (1) it requires a smaller quantity of gas, which is thus more easily procured in a state of great dryness and purity, and (2) it minimises errors due to (a) buoyancy corrections, (b) shrinkage, (c) adsorption of moisture on the outside of the globe, and (d) adsorption of gas on the inside of the globe.

The general gas law.—On p. 49 it has been shown that for a given mass of an ideal gas the equation :

$$pv/T = \text{const.}, \text{ or } pv = \text{const. } T,$$

applies, where p = pressure, v = volume, T = absolute temperature. If the mass is 1 gm. mol. wt., or 1 mol, Avogadro's hypothesis shows that

v is the same for all gases for the same values of p and T . This value of v has been shown to be 22.4 litres when $p=1$ atm. and $T=273$ (i.e. 0°C). Hence the gas constant, which applies for all other values of p and T for 1 mol of gas and is denoted by R , is

$$R = 1 \times 22.4/273 = 0.082 \text{ litre atmospheres/}1^\circ\text{C.},$$

and

$$pv = RT.$$

R has the dimensions of energy divided by temperature, since (pressure \times volume) has the dimensions of work.

Calculations of volumes of gases.—Avogadro's hypothesis shows that the molecular volume of *any* gas at S.T.P. is 22.4 litres. In calculations of volumes of gases, the chemical equations must be written so as to express reactions between *molecules* of the gases, since only in this case are the volume relations correctly given.

For any arbitrary weight of gas, W gm., the number of mols is $n = W/M$, where M is the molecular weight. If the volume is V , the molar volume is V/n . Hence, in general:

$$pV = nRT \text{ for } n \text{ mols of gas.}$$

It is important to remember that $pv = RT$, with the value of R stated, applies only to *one mol* of gas. In general calculations $pV = nRT$ must be used. *E.g.* to find the volume of 100 gm. of chlorine at 15° and 410.4 mm.: $T = 273 + 15 = 288$; $p = 410.4/760 = 0.54$ atm.: $n = 100/71 = 1.408$ mols:

$$\therefore V = nRT/p = 1.408 \times 0.082 \times 288/0.54 = 61.6 \text{ litres.}$$

Cannizzaro's principle.—Avogadro did not clearly state that molecular weights must be referred to the *atom*, not the molecule, of hydrogen as standard. This step was taken in 1858 by Cannizzaro, who showed that Avogadro's hypothesis can be systematically applied in the determination of atomic weights.

(1) From vapour density measurements the *molecular weights* of a number of volatile compounds of an element are found.

(2) The analyses of these compounds give the weights of the element contained in the molecular weights of the compounds.

(3) The smallest of these weights is taken as the atomic weight, it being assumed that at least one compound contains only one atom of the given element in its molecule.

The atomic weight of an element is the smallest weight of the element contained in a molecular weight of any of its compounds.

This may be called **Cannizzaro's principle**: it is not an independent definition of atomic weight, but is a consequence of Avogadro's hypothesis.

It must be emphasised that the determination of the relative density of *one* compound of an element, or of the *element itself* if it is volatile, can give no sure indication of the atomic weight. The molecule of the particular compound selected, and that of the vapour of the free

element, may contain one, two, three, or any number of atoms of the element, for all we know to the contrary. In the case of mercury, the molecule in the vapour consists of one atom, and the molecule of phosphorus vapour contains four atoms. The larger the number of compounds investigated, the greater is the probability that at least one will contain only one atom of the element in a molecule.

OXYGEN COMPOUNDS.

Compound.	Rel. Density (H = 1) Δ	Mol. wt. $- 2 \times \Delta$	Wt. of oxygen in one mol. wt. of compound
Oxygen gas - - -	16	32	16×2
Water - - - - -	9	18	16
Carbon monoxide - - -	14	28	16
Carbon dioxide - - -	22	44	16×2
Sulphur dioxide - - -	32	64	16×2
Sulphur trioxide - - -	40	80	16×3
Nitrous oxide - - -	22	44	16
Nitric oxide - - -	15	30	16

The smallest weight of oxygen contained in a molecular weight of any of these compounds is 16, and this is taken as the atomic weight. A molecule of water contains one atom of oxygen, weight 16, and therefore $18 - 16 = 2$ parts, or two atoms, of hydrogen. The formula of water is therefore H_2O . In this way, Dalton's problem of finding the number of atoms of the elements in the molecule of a compound is easily solved.

CARBON COMPOUNDS.

Compound.	Rel. Density (H = 1) Δ	Mol. wt. $- 2 \times \Delta$	Wt. of carbon in one mol. wt. of compound.
Methane - - - - -	8	16	12
Ethane - - - - -	15	30	12×2
Ethylene - - - - -	14	28	12×2
Alcohol - - - - -	23	46	12×2
Ether - - - - -	37	74	12×4
Benzene - - - - -	39	78	12×6
Carbon monoxide - - -	14	28	12
Carbon dioxide - - -	22	44	12

The atomic weight of carbon deduced from these results is 12. In 78 parts of benzene there are 72 parts, or 6 atoms, of carbon and $78 - 72 = 6$ parts, or 6 atoms, of hydrogen. The formula of benzene is C_6H_6 .

The molecular weights found from the densities are *approximate*, since gases and vapours do not accurately obey the gas laws, and the determinations may be approximate. *Accurate* values of the atomic and molecular weights are found from refined chemical analyses of the compounds, and vapour density measurements are used to decide between various possible molecular weights. Accurate values are found from limiting densities (p. 105).

In some cases an element does not form volatile compounds, so that Cannizzaro's method cannot be applied. Alternative methods must then be used, which are described in the next section.

Confirmation of atomic weights.—The atomic weights derived from Cannizzaro's principle have been confirmed by independent methods. These remove the possibility that the least weight of an element found in the molecular weights of all the compounds examined may still be a multiple of the atomic weight, since it is improbable that *all* the independent methods should agree with this particular multiple. These methods will be considered in more detail later and a summary only is given here.

1. Molecular weights of substances in solution, found by osmotic pressure, freezing point, boiling point or vapour pressure methods, usually agree with those found from vapour densities. In some cases, *e.g.* metals in amalgams, the molecular weight is identical with the atomic weight.

2. The ratio of the specific heats of a gas or vapour at constant pressure c_p , and at constant volume c_v , viz. c_p/c_v , according to the kinetic theory of gases, has the value 1.667 when the molecule is *monatomic*. In 1876 Kundt and Warburg found that $c_p/c_v = 1.667$ for mercury vapour, hence the molecules of the latter consist of single atoms. The density of mercury vapour shows that the molecular weight is 200. This in the present case is equal to the atomic weight. If the atomic weight found by the vapour density method is shown in one case, viz. mercury, to be the real atomic weight and not a multiple, it may reasonably be assumed that in other cases also the method gives the real atomic weights. In the case of many *diatomic* gases, the theoretical ratio $c_p/c_v = 1.4$ is found.

3. Dulong and Petit in 1819 found that the *atomic heat*, *i.e.* the product of the atomic weight and the specific heat of a solid element, is approximately constant and equal to 6.3. Hence if the specific heat of a solid element is determined, and 6.3 is divided by this number, we obtain an *approximate* value of the atomic weight. This does not give correct results with elements of small atomic weight.

4. Mitscherlich in 1819 found that compounds having analogous formulae crystallise in the same form or are *isomorphous*. Thus the formulae of isomorphous compounds can be found and hence, by analysis, the atomic weights of their elements. In some cases a substance may crystallise in more than one form, and this must be kept in mind in using the method.

5. The formulae of compounds which show similarities in chemical properties are usually similar. Oxides of iron, aluminium and chromium are given similar formulae, Fe_2O_3 , Al_2O_3 and Cr_2O_3 . If the atomic weight of chromium is found, those of aluminium and iron can be determined. This method is the least trustworthy of all those described; *e.g.* beryllium oxide was long thought to be Be_2O_3 instead of BeO on the basis of chemical analogies.

6. The position of an element in the periodic table (Chapter XXII) gives an indication of its atomic weight.

Diffusion of gases.—Hydrogen contained in an open *inverted* jar rapidly diffuses out and air enters; this takes place in opposition to gravity since hydrogen, the lighter gas, moves downwards and air, the

heavier gas, moves upwards. Döbereiner (1823) found that hydrogen confined over water in a cracked flask escaped into the surrounding air, the water rising in the neck of the flask. Graham (1831) showed that as the hydrogen escapes air enters the flask, and since the pressure inside is reduced hydrogen must diffuse out faster than air diffuses in. If the flask is covered with a bell-jar filled with hydrogen no change in the level of water occurs.

The diffusion of gases may be illustrated by the apparatus shown in Fig. 64. A porous clay pot such as is used in batteries is fitted by a rubber bung to a tube passing into a Woulfe's bottle containing coloured water. Dipping into the coloured water is a glass tube drawn out to a jet above.

A large beaker of hydrogen is inverted over the pot, when hydrogen diffuses into the pot more rapidly than air passes out and the increase of pressure causes the water to issue from the jet in the form of a fountain.

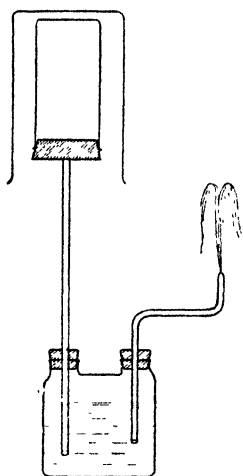


FIG. 64.—Diffusion of hydrogen through a porous pot.



FIG. 65.—Graham's apparatus.

If the beaker is removed, hydrogen inside the pot diffuses out into the air more rapidly than air enters, so that the pressure is reduced. Coloured water thus rises in the vertical tube attached to the pot.

Graham's law.—Graham's apparatus for measuring the rates of diffusion of gases consists of a glass tube closed at one end with a thin plug of plaster of Paris. This tube is filled with hydrogen over mercury (Fig. 65). The mercury rises in the tube, which is sunk so as to keep the levels constant. After a certain time all the hydrogen diffuses out and the tube contains only air which has diffused in. The volume of this air is the volume diffusing in the same time as the whole of the hydrogen originally contained in the tube. The inverse ratio of these volumes

gives the ratio of the *times* required for the diffusion of equal volumes. In this way Graham in 1833 found the following law of diffusion: *the rate of diffusion of a gas is inversely proportional to the square root of its density.*

Since the density D at a fixed temperature and pressure is proportional to the molecular weight M , Graham's law shows that *the velocity of diffusion of a gas is inversely proportional to the square root of its molecular weight.*

EXAMPLE 1.—100 ml. of hydrogen are confined in a diffusion tube exposed to air. When change of volume ceases, what volume of air will have entered the tube?

The volumes diffusing are in the inverse ratio of the square roots of the densities ;

$$\therefore \frac{\text{volume of hydrogen}}{\text{volume of air}} = \frac{\sqrt{1.293}}{\sqrt{0.09}}$$

$$\therefore \text{vol. of air} = 100 \cdot \frac{\sqrt{0.09}}{\sqrt{1.293}} = 26.4 \text{ ml.}$$

EXAMPLE 2.—16.8 ml. of chlorine diffused in the same time as 100 ml. of hydrogen. Find the relative density of chlorine.

Let x = relative density of chlorine. The volumes diffusing in equal times are in the inverse ratio of the square roots of the densities. Since the relative density of hydrogen is 1,

$$\therefore \frac{100}{16.8} = \frac{\sqrt{x}}{\sqrt{1}} = \sqrt{x};$$

$$\therefore x = 35.4.$$

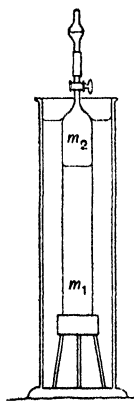


FIG. 66.—Bunsen's effusio-meter (Ostwald).

the tube is a stopcock communicating with the free air through a tube closed by a thin platinum plate, in which a hole has been pierced with a fine needle. The tube is filled with gas to a level below m_1 and the tap is opened. The gas streams out through the fine hole and the time required for the liquid surface to pass from m_1 to m_2 is taken by a stop-watch. The experiment is repeated with a gas of known molecular weight, *e.g.* oxygen. If mercury is used, a float is fitted inside the tube, having a line marked

Effusion.—In effusion (also studied by Graham) a gas is forced by pressure through a small hole in a metal plate exposed to the air. *The relative rates of effusion of different gases are in the inverse ratio of the square roots of the densities.* By means of this law the molecular weights of different gases may be compared. The apparatus used is Bunsen's effusimeter.

A glass cylinder with marks at m_1 , m_2 is placed in a cylinder of water (Fig. 66.) At the top of

on its upper end. The time taken for this mark to pass between two marks on the upper surface of the cylinder is noted

If t_1, t_2 are the times of effusion of equal volumes of two gases of densities D_1, D_2 and molecular weights M_1 and M_2 in the same apparatus, then :

$$\frac{t_1}{t_2} = \frac{\sqrt{D_1}}{\sqrt{D_2}} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$$

EXAMPLE.—If the times of equal effusion of pure oxygen and of a mixture of oxygen and ozone are 224 and 234 seconds, respectively, find the percentage by volume of ozone in the mixture.

Let D = relative density (O = 16) of the mixture, and x = percentage of ozone (O_3). Then

$$\frac{224}{234} = \frac{\sqrt{16}}{\sqrt{D}}, \quad \therefore D = 17.46.$$

$$16 \left(\frac{100-x}{100} \right) + 24 \left(\frac{x}{100} \right) = 17.46, \quad \therefore x = 18.25.$$

Abnormal vapour densities.—Acetic acid has the empirical formula (the simplest formula deduced from its percentage composition) CH_2O . Its vapour density at 250° and 760 mm. pressure is 29 ($H = 1$), hence the molecular weight is 58. But $C_2H_4O_2 = 60$, hence under these conditions the vapour has this formula. At lower temperatures, at 760 mm. pressure, the density is greater; at 125° it is 44.5, corresponding with a molecular weight of 89, which approximates to $C_3H_6O_3 = 90$.

Playfair and Wanklyn (1862) explained this apparent exception to Avogadro's law by assuming that the vapour of acetic acid below 250° is a mixture of $C_2H_4O_2$ molecules with $C_4H_8O_4$ molecules, *i.e.* the substance is associated. By rise of temperature, some of the associated molecules break up into normal molecules: $(C_2H_4O_2)_2 = 2C_2H_4O_2$. (This also occurs if the pressure is reduced at a constant temperature).

A different behaviour is shown by ammonium chloride. The solid has the simplest formula $NH_4Cl = 53.5$. Bineau found the vapour density 12.9, giving a molecular weight of 25.8, half the least possible theoretical value, and corresponding with the formula $N_2H_2Cl_2$. This and similar cases (phosphorus pentachloride, ammonium carbamate, etc.) led Deville to question the validity of Avogadro's law, but the true explanation was put forward independently by Cannizzaro in 1857, and by Kopp and Kekulé in 1858, *viz.* that these substances dissociate on heating.

Dissociation by heat.—Mitscherlich in 1833 observed that antimony pentachloride vapour on heating is partly dissociated into antimony trichloride and free chlorine: $SbCl_5 = SbCl_3 + Cl_2$. These recombine on cooling. Since the reaction is reversible it may be written $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$. Reactions of this type are examples of **thermal dissociation**, *i.e.* the progressive decomposition of a compound by heat, in such a way that the products of decomposition recombine on cooling. They

differ from such reactions as the decomposition of potassium chlorate by heat, when the products do not recombine on cooling.

J. H. Gladstone (1849) found that the pale yellow solid phosphorus pentabromide partly dissociates when heated into the vapour of the tribromide (colourless) and free bromine (red) : $\text{PBr}_5 \rightleftharpoons \text{PBr}_3 + \text{Br}_2$. The vapour is red, and in an open flask bromine diffuses out and the denser PBr_3 remains.

It was therefore reasonable to assume that ammonium chloride on heating dissociates into ammonia and hydrogen chloride which recombine on cooling : $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$. The density for complete decomposition is half the theoretical density, because the volume is doubled. Pebal (1862) confirmed this by separating the two gases from the vapour by diffusion. Ammonia is much lighter than hydrogen chloride and diffuses more rapidly (p. 112).

Pebal used the apparatus shown in Fig. 67. The tube *D* contained a plug of asbestos *c*, and above this was a piece of ammonium chloride *d*. The tube was enclosed in a wide test-tube, contained in a jacket heated in a

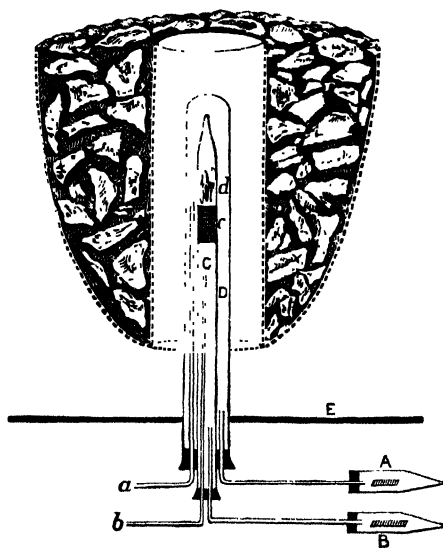


FIG. 67.—Pebal's experiment on the dissociation of ammonium chloride

charcoal furnace. Hydrogen was passed in through the tubes *a*, *b*, on both sides of the plug, and escaped through tubes to *A* and *B*, containing pieces of blue and red litmus paper, respectively. The red litmus turned blue, because ammonia escaped more rapidly through the asbestos plug than hydrogen chloride; the excess of the latter was swept out through the other tube, and turned the litmus red.

Deville objected that the vapour might have been decomposed by the asbestos plug. Than (1864), replaced the asbestos by a plug of solid ammonium chloride (Fig. 68) and obtained the same result.

Marignac (1868) showed that the absorption of heat required to volatilise ammonium chloride is practically equal to the heat evolved when the gases ammonia and hydrogen chloride combine to form solid ammonium chloride, and hence the compound must decompose into the two gases on volatilisation.

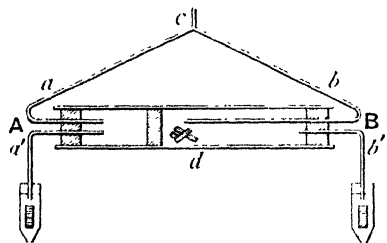


Fig. 68. - Than's experiment on the dissociation of ammonium chloride.

Some ammonium chloride is put into a glass tube through which passes a porous clay tobacco-pipe stem (Fig. 69). On heating, the ammonium chloride dissociates into ammonia and hydrogen chloride gases. The ammonia diffuses more rapidly through the porous tube, leaving in the glass tube an excess of hydrogen chloride, which reddens a piece of blue litmus paper. By

passing a *slow* current of air through the clay tube, the gas containing excess of ammonia is directed on a piece of moist red litmus paper, which becomes blue.

In dissociation, a state of chemical equilibrium is established, in which the dissociating substance and the products of dissociation exist together. The extent of dissociation increases with rise of temperature, as is seen, for example, in the progressive darkening in colour of the vapour of

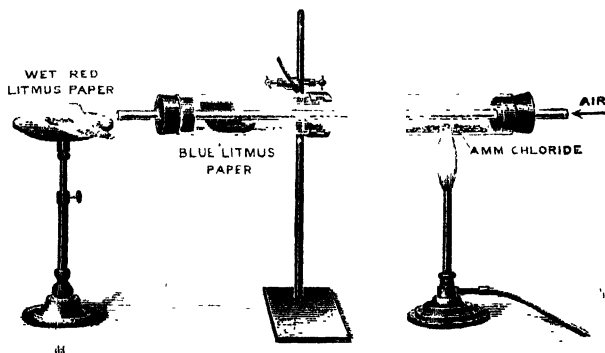


Fig. 69. - Dissociation of Ammonium Chloride.

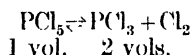
phosphorus pentabromide, owing to the formation of red bromine vapour: $\text{PBr}_5 \rightleftharpoons \text{PBr}_3 + \text{Br}_2$. The dissociation of colourless hydrogen iodide gas on heating is seen from the violet colour of the iodine vapour produced: $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$. In this case the products of dissociation

tion do not recombine completely on cooling, solid iodine separating, but the reaction is reversible in presence of a catalyst (p. 142).

Both PCl_5 and PCl_3 are colourless in the form of vapour; Cl_2 is greenish-yellow. The vapour of PCl_5 shows a greenish-yellow colour, which becomes deeper as the temperature increases. At the same time the density (reduced to S.T.P.) decreases.

Determination of dissociation from vapour density.—The degree of dissociation α , *i.e.* the fraction of the total number of molecules dissociated, can be deduced from the vapour density, except where there is no change of volume on dissociation, *e.g.* $\text{HI} + \text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$.

In the dissociation of substances such as phosphorus pentachloride, when a change of volume occurs :



let each molecule of the initial substance give x molecules on dissociation. Then N molecules of substance give :

$N(1 - \alpha)$ molecules of original substance,
 $Nx\alpha$ molecules of the products of dissociation.

The number of molecules before dissociation is N ; that after dissociation is $N(1 - \alpha) + Nx\alpha = N[1 + \alpha(x - 1)]$, and by Avogadro's law :

$$\frac{\text{Volume after dissociation}}{\text{Volume before dissociation}} = \frac{N[1 + \alpha(x - 1)]}{N} = 1 + \alpha(x - 1).$$

The densities are in the inverse ratio of the volumes. Let Δ be the vapour density corresponding with the undissociated substance, and D the observed vapour density, then :

$$\frac{\Delta}{D} = 1 + \alpha(x - 1)$$

$$\therefore \alpha = \frac{\Delta - D}{D(x - 1)}.$$

The vapour density corresponding with complete dissociation ($\alpha = 1$) is $d = \Delta/x$. In the case of phosphorus pentachloride, $x = 2$, hence : $\alpha = (\Delta - D)/D$, and $d = \frac{1}{2}\Delta$, *i.e.* on complete dissociation the vapour density has half the normal value.

The vapour densities may be in any units, *e.g.* gm./lit., or relative to $\text{H} = 1$, or air = 1, etc.. In the following table of vapour densities of phosphorus pentachloride at 1 atm. pressure (Cahours, 1847) the density D is relative to oxygen taken as 16, so that $2D \cdot M$ = apparent molecular weight.

At 200° and 1 atm. pressure, the vapour density of phosphorus pentachloride is 70.03 (O = 16). The density corresponding with no dissociation is $\frac{1}{2}\text{PCl}_5 = 103.35$. Thus, $\Delta = 103.35$, $D = 70.03$, $x = 2$, and $\alpha = \frac{103.35 - 70.03}{70.03} = 0.476$. Out of every 1000 molecules of PCl_5 , 476 are dissociated into $\text{PCl}_3 + \text{Cl}_2$.

t° -	182	190	200	230	250	274	288	300
D -	73.36	72.06	70.03	69.21	57.77	55.46	53.01	52.71
α -	0.409	0.434	0.476	0.493	0.788	0.864	0.950	0.961

A molecular theory of dissociation was given by Pfaundler in 1867. In a molecule such as HI the atoms are vibrating, the energy and hence the amplitude of vibration increasing with rise of temperature. The temperature depends (p. 120) on the kinetic energy of translation of the molecules, but this is partly transformed by collisions into vibrational energy. When the amplitude of vibration exceeds a limiting value, the atoms part company and dissociation occurs. The reason why all the molecules do not dissociate suddenly and completely at a particular temperature, is that a gas at a certain temperature contains molecules with all possible kinetic energies, the *average* kinetic energy corresponding with the temperature of the gas. Those molecules with energies higher than the average tend to dissociate, and since the fraction of these molecules with high energies increases with rise in temperature, according to Maxwell's distribution law (p. 119), the extent of dissociation increases with rise in temperature. The products of dissociation are at the same time recombining, and at a fixed temperature a state of equilibrium is reached, when as many molecules are decomposed as are formed in a given interval of time.

CHAPTER X

THE KINETIC THEORY OF GASES

The kinetic theory of gases.—Dalton in 1801 filled two bottles (Fig. 70), one with hydrogen and the other with carbon dioxide, and connected them by a long vertical glass tube, the light gas being above. After several hours the gases were uniformly mixed. This spontaneous mixing of gases in opposition to gravity is called *diffusion*, and is due to the *motion of the molecules* of the gases amongst each other.



FIG. 70. — Dalton's experiment on gaseous diffusion.

Similar motions occur in liquids, but even more slowly. If a tall cylinder is filled with water, and a layer of copper sulphate crystals placed at the bottom (Fig. 71), a layer of blue solution is formed. If the jar is set aside in a room of uniform temperature, to avoid convection currents, the blue colour slowly rises through the jar until, after several months, the colour of the liquid is uniform.

We assume that the molecules of liquids and gases are in ceaseless motion, in much the same way as a swarm of gnats on a summer evening. This is called the *kinetic theory* (Greek *kinesis*, motion).

From the slowness of diffusive motion it might seem that the molecular velocities must be small. This is not correct: the molecules in air, for example, move with speeds of the order of a quarter of a mile per second. In the same way the gnats in a swarm move about with considerable speeds, although the swarm itself is nearly stationary.

The cause of gaseous pressure.—Joule in 1845 found that if a gas expands from one vessel into a second exhausted copper vessel, so that it does no external work, it does not become appreciably warmed or cooled. He concluded that no appreciable work is done by, or against, forces of repulsion or attraction between the molecules, and hence that *the molecules of gases exert practically no forces on one another*.

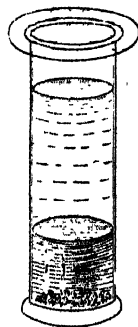


FIG. 71.—Liquid diffusion.

The pressure exerted by a gas over the walls of a vessel must, therefore, be caused by molecular bombardment. On all parts of the surface

there is a ceaseless hail of elastic molecules, which fly off again into the gas. Without going into detail one can see that this molecular bombardment, distributed over the surface, must appear as a uniform pressure.

The molecules strike the wall at all angles, from a full normal blow to a glancing impact, and it is only the velocity component perpendicular or normal to the surface which is effective in producing pressure.

In the gas itself the molecules exert practically no forces one upon another, and move in straight lines until they encounter the walls, or one molecule collides with another. The molecular collisions occupy but a small fraction of the time in which the molecule is moving, because the particles are sparsely distributed, except in highly compressed gases.

One ml. of water gives 1240 ml. of vapour at 100° and 760 mm. pressure, so that less than one-thousandth of the space of the vapour is occupied by the molecules. In air at 0.001 mm. pressure, the molecules occupy only about 1 part in 580 millions of the total space.

The molecules may have all possible velocities, but Clerk Maxwell (1859) showed that most of the molecules in a gas at a given temperature have velocities which differ only slightly from a *mean* or *average velocity* \bar{c} . The ordinates of the curve in Fig. 72 represent the fractions of the molecules which have velocities represented by the abscissae as multiples of the *most probable velocity*, 0.886 \bar{c} . If we follow *any* molecule along its zigzag path, we shall find that they nearly all have velocities very near the average velocity \bar{c} . The *component* velocities fluctuate repeatedly as the molecules undergo collisions, but the velocity along the path of motion is nearly uniform.

The curve in Fig. 72 represents what is called *Maxwell's distribution law*.

Calculation of the pressure of a gas.—Let a mass M of gas be contained in a cube of side L , and let c be the velocity of the molecules, assumed provisionally to be the same for all. Let there be N particles in a unit cube, or NL^3 in the given cube. We may suppose

that on the average one-third of the particles, *i.e.* a number $NL^3/3$, are moving (in both directions) perpendicular to each pair of faces. The number of impacts per second made by a particle on any one face is $c/2L$, since it traverses a distance $2L$ between each impact with that face. The total number of impacts per second on the face is $(c/2L) \times (NL^3/3) = NcL^2/6$. The momentum of the molecule, of mass m , before impact is mc ; after impact it is $-mc$, hence the change of

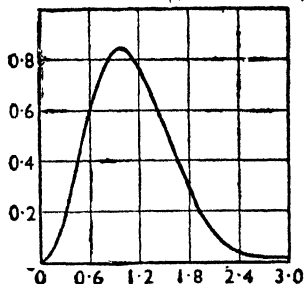


FIG. 72.—Distribution of molecular speeds in a gas.

momentum is $2mc$. The change of momentum per second is the force exerted on the face. The *pressure*, or force per unit area, due to all the particles is, therefore, $(NcL^2/6) \times (2mc) : L^2$, where L^2 is the area of the face. Thus:

$$p = \frac{1}{3}mNc^2.$$

But $mN = M/L^3 = M/V = D =$ density of the gas, therefore :

$$p = \frac{1}{3}Dc^2 \quad \text{or} \quad pV = \frac{1}{3}Mc^2. \dots\dots\dots(1)$$

If groups of N_1, N_2, N_3, \dots molecules move with different velocities c_1, c_2, c_3, \dots , the above calculation applies to each group separately, and by summation :

$$p = \frac{1}{3}m(N_1c_1^2 + N_2c_2^2 + N_3c_3^2 + \dots).$$

If a *mean square velocity* \bar{c}^2 is taken such that :

$$N\bar{c}^2 = N_1c_1^2 + N_2c_2^2 + N_3c_3^2 + \dots$$

where $N = N_1 + N_2 + N_3 + \dots$, *i.e.* $\bar{c}^2 = \Sigma N_1c_1^2 / \Sigma N_1$, then :

$$p = \frac{1}{3}mN\bar{c}^2 = \frac{1}{3}D\bar{c}^2 \quad \text{or} \quad pV = \frac{1}{3}M\bar{c}^2. \dots\dots\dots(1a)$$

The *mean or average velocity* \bar{c} is related to the root mean square velocity by the formula :

$$\bar{c} = \frac{4}{\sqrt{6\pi}} \sqrt{c^2} = 0.921 \sqrt{c^2}. \dots\dots\dots(2)$$

If \bar{u} is the average *component* velocity normal to the wall of the vessel, half the molecules may be supposed to be moving towards the wall with this velocity and half away from it. Hence the number of molecules striking 1 cm² of wall per sec. is half the number in a cylinder of height \bar{u} , *viz.* $\frac{1}{2}N\bar{u}$, and the mass of gas striking 1 cm² per sec. is $\frac{1}{2}mN\bar{u} = \frac{1}{2}D\bar{u}$.

Deduction of the gas laws.—The average kinetic energy of translation of a molecule is $\frac{1}{2}m\bar{c}^2$, hence equation (1) or (1a) shows that : *the product of the pressure and volume of a gas is equal to two-thirds of the kinetic energy of translation of the molecules.* The kinetic energy of translation is the energy the molecules possess in virtue of their motion in straight lines ; only this part of the energy makes any contribution to the pressure. Energy due to rotation of the molecules, or the relative motions of their parts, is without influence.

If it is assumed that *the absolute temperature of the gas is proportional to the average translational kinetic energy of the molecules*, equation (1) or (1a) shows that, when the temperature is constant, the pressure is proportional to the density or inversely proportional to the volume. This is Boyle's law.

Since the absolute temperature T is assumed to be proportional to the average translational kinetic energy of the molecules, *i.e.* to $\frac{1}{2}m\bar{c}^2$, it follows from (1a) that at constant volume ($N = \text{const.}$) :

$$p = \text{const.} \times T,$$

which is equivalent to Charles's Law.

If equal volumes of two gases at the same temperature and pressure contain N_1 and N_2 molecules of masses m_1 and m_2 , respectively :

$$p = \frac{1}{3}N_1m_1\overline{c_1^2} = \frac{1}{3}N_2m_2\overline{c_2^2} \text{ (pressures equal)}$$

and $\frac{1}{2}m_1\overline{c_1^2} = \frac{1}{2}m_2\overline{c_2^2}$ (temperatures equal),

hence $N_1 = N_2$,

which is Avogadro's hypothesis.

For two gases of the same temperature :

$$\frac{1}{2}m_1\overline{c_1^2} = \frac{1}{2}m_2\overline{c_2^2};$$

$$\therefore c_1/c_2 = \sqrt{m_2/m_1} = \sqrt{D_2/D_1},$$

or the molecular velocities are inversely proportional to the square roots of the molecular weights or densities. Since the velocity of diffusion may be assumed to be proportional to the molecular velocity, this is equivalent to Graham's law of diffusion (p. 111). The diffusion rate however, involves the mean free path (p. 123) as well as the molecular velocity and the quantitative relation is rather complicated.

Molecular kinetic energy.—In equation (1a) put $V = 22.415$ litres, then at S.T.P. $M = \mathbf{M}$, the gram-molecule (mol) of the gas and $N = \mathbf{N}$, the number of molecules in a gram-molecule. \mathbf{N} is called Avogadro's number. Avogadro's hypothesis shows that \mathbf{N} is the same for all gases. We see that the kinetic energy of translation of the molecules is :

$$\frac{1}{2}\mathbf{M}\overline{c^2} = \frac{3}{2}pV = \frac{3}{2}\mathbf{R}T \dots \dots \dots (3)$$

It is the same for a mol of any gas at a given temperature. We can now calculate this energy.

At the melting point of ice, $V = 22.415$ litres = 22.415×1000.028 cm.³,
 $p = 760$ mm. = $76 \cdot 13.595 \times 980.6 = 1,013,225$ dynes per cm.² ;

$$\therefore \frac{3}{2}pV = 22.415 \times 1000.028 \times 1013225 \times \frac{3}{2} = 3.407 \cdot 10^{10} \text{ ergs.}$$

Thus, the molecular kinetic energy of a mol of any gas at 0°, due to the translatory motion of its molecules, is large enough to raise a weight of about a ton through one foot.

The gas constant is :

$$\mathbf{R} = pV/T = \frac{3}{2} \times 3.407 \cdot 10^{10} / 273.09 ;$$

$$\therefore \mathbf{R} = 8.317 \times 10^7 \text{ ergs/1}^\circ \text{C. ;}$$

$$\text{or } \mathbf{R} = 8.317 \times 10^7 / 4.184 \times 10^7$$

$$= 1.988 \text{ g. cal./1}^\circ \text{C.}$$

Molecular velocities.—From the value of the molecular translational kinetic energy $\frac{1}{2}\mathbf{M}\overline{c^2}$, which is the same for all gases and equal (very approximately) to 34×10^9 ergs at 0°, we can calculate the mean square molecular velocities, $\overline{c^2}$, by division by the molecular weight \mathbf{M} and multiplication by 2 :

$$\overline{c^2} = (\frac{1}{2}\mathbf{M}\overline{c^2}) \times 2/\mathbf{M}.$$

Thus, for oxygen, $M = 32$; $\therefore \bar{c}^2 = 34 \times 10^9 \times 2/32$; \therefore the root mean square velocity $\sqrt{\bar{c}^2}$ at $0^\circ \text{C.} = 46,000 \text{ cm. per sec.}$, or 460 m. per sec. The average velocity \bar{c} is $0.921 \sqrt{\bar{c}^2}$, from equation (2), *i.e.* 425 m. per sec. In the case of hydrogen, the average velocity at 0° is 1694 m. per sec.

AVERAGE MOLECULAR VELOCITIES AT 0 IN METRES PER SECOND

(Velocities of sound in the gases are given in brackets.)

Hydrogen, 1694 (1286).	Oxygen, 425 (317).
Helium, 1208.	Carbon dioxide, 362 (257).
Steam, 565 (401).	Chlorine, 288 (206).
Nitrogen, 455 (337).	Mercury vapour, 170.

The velocity of steam molecules ($M = 18$) is greater than that of oxygen molecules ($M = 32$); the velocities for hydrogen and helium are large compared with those of the other gases. A velocity of 1700 m. per sec. is 5500 ft. per sec., or more than a mile per sec., *i.e.* of the order of the velocity of a rifle bullet. Owing to these high speeds the kinetic energies of the molecules are high, and the pressure due to the molecular shower is explained. It is also seen that the molecular velocities are of the same order as, but greater than, the velocities of sound u in the gases. The formulae $p = \frac{1}{3} D \bar{c}^2$ and $u = \sqrt{\gamma p / D}$ ($\gamma = c_p / c_v$), give $u = \sqrt{\frac{1}{3} \gamma} (\sqrt{\bar{c}^2})$.

The product pV for a given mass of gas is proportional to the absolute temperature: $pV = RT$. But pV is proportional to the translational kinetic energy of the gas molecules, hence the latter is also proportional to the absolute temperature. Since at constant volume the pressure increases by 1.273 of its value at 0°C. for 1° rise in temperature, the translational kinetic energy of the molecules must increase by the same fraction of its value at 0°C. In this way we can calculate the molecular velocities at any temperature from their values at 0°C. given in the table.

For hydrogen molecules at 1000°C. : kinetic energy at $1000^\circ = (1273/273) \times$ kinetic energy at 0°C. But the average velocity is proportional to $\sqrt{(\text{kinetic energy})}$;

$$\therefore \text{velocity at } 1000^\circ : \text{velocity at } 0^\circ = \sqrt{1.273} : \sqrt{.273};$$

$$\therefore \text{velocity at } 1000^\circ = 1694 \times \sqrt{\frac{1.273}{.273}} = 1694 \times 2.16 \text{ m. per sec.}$$

The rate of increase of velocity with temperature is not very rapid; the velocity is doubled by a rise of 1000° .

For a gram-molecule, $pv = RT$. The kinetic energy of translation of the molecules is $\frac{1}{2} M \bar{c}^2 = \frac{3}{2} pV = \frac{3}{2} RT$. The value of R in absolute units is 8.317×10^7 ergs per 1° , hence the translational kinetic energy at T° absolute is $\frac{3}{2} \times 8.317 \times 10^7 T$ ergs = $12.476 \times 10^7 T$ ergs. In g. cal. it is $\frac{3}{2} \times 1.988 T = 2.982 T$ g. cal., or about 3 T g. cal.

The molecular diameter.—In spite of the high values of the molecular velocities the diffusion of one gas into another takes place slowly.

The experiment on p. 54 shows that bromine vapour diffuses very slowly, although at 17° the velocity of the bromine molecules must be :

$$1700 \times \sqrt{(290/273)} \times \sqrt{(1/80)} = 196 \text{ metres per sec.},$$

where 1700 m. per sec. is the velocity of hydrogen molecules, and the velocities are in the inverse ratio of the square roots of the molecular weights (2 and 160). The rate of bulk motion of bromine vapour is only about one hundred thousandth of the molecular velocity.

The reason is that the molecules of bromine do not move all the time in straight lines ; they collide with one another and with the air molecules, and very many must be deflected back again. The molecules describe zigzag paths, and only after making a great number of collisions does a molecule get appreciably forward.

This effect is due to the finite size of the molecules : if they were mere points, they would not offer any obstacles to the motion of other molecules. From the rate of diffusion the diameters of molecules may be calculated ; the diameter of the oxygen molecule, assumed spherical, is about 3×10^{-8} cm. = 3Å . ($\text{Å} = \text{Ångström unit} = 10^{-8}$ cm.).

Platinum wires can be drawn to 10^{-4} cm. in diameter ; ordinary gold-leaf is 10^{-5} cm. thick ; the black parts of soap-films are 6×10^{-7} cm. thick, and oil-films on water are only 10^{-7} cm. thick, or less.

The distance of the nearest fixed star is reckoned in light-years, 1 light-year being the distance traversed by light (3×10^{10} cm./sec.) in a year, or 10^{18} cm. It is incorrect to regard the minuteness of molecules as a counterpart of the vast interstellar distances. The molecules are small, it is true—too small to be visible (when their presence would be confusing), but their refinement has not been overdone.

The mean free path.—The average distance traversed by a gas molecule before collision with another is called its mean free path, L . This can be calculated from the viscosity η , of the gas, by the formula : $L = 1.25\eta/\sqrt{pD}$. Since the density D is proportional to the pressure p , the mean free path is inversely proportional to the pressure (η is independent of p). It is greater the lower the pressure, because the molecules are then less crowded together. From the mean free path the molecular diameter d is calculated by Maxwell's formula

$$L = \frac{1}{\sqrt{2}\pi N d^2}, \dots\dots\dots(4)$$

where N = number of molecules per ml. (*Loschmidt's number*.)

In oxygen at S.T.P., L is very nearly 10^{-5} cm. ; it is double this in hydrogen. At low pressures, e.g. in the space between the walls of a "thermos" flask, the free path is several cm., and a molecule rebounds from the opposite walls many times without encountering another.

Molecular collision frequency.—During one second a molecule describes as many free paths as it makes collisions, and the sum of the paths is equal to the average velocity \bar{c} . Thus, the number of collisions of one molecule with others per second is \bar{c}/L . In oxygen this is $4.25 \times 10^4/10^{-5} = 4.25 \times 10^9$. At very low pressures the mean free path

is 1 cm., but even then there will be 10^5 , or 100,000 collisions per second.

If there are N molecules per cm.³ the number of collisions of all the molecules per cm.³ per sec. (the collision frequency) is $\frac{1}{2}N\bar{c}/L = \frac{1}{\sqrt{2}}N^2\pi d^2\bar{c}$.

(The factor $\frac{1}{2}$ is inserted because in taking all the N molecules each collision is counted twice, each molecule being counted as making a collision with another and as being struck by the second one.)

Since from equation (3) :

$$\frac{1}{2}M\bar{c}^2 = \frac{3}{2}pV = \frac{3}{2}RT$$

and from equation (2) :

$$\bar{c} = \frac{4}{\sqrt{6\pi}} \sqrt{\bar{c}^2}$$

it follows that :

$$\bar{c} = \sqrt{(8RT/\pi M)}, \dots\dots\dots(5)$$

where $R = 8.3 \times 10^7$ erg./1°. Hence the total number of molecular collisions per cm.³ per sec. is

$$Z_1 = 2N^2d^2\sqrt{\pi RT/M}, \dots\dots\dots(6)$$

For two different kinds of molecules the number of collisions per cm.³ per sec. is given by

$$Z_{12} = \pi \left(\frac{d_1 + d_2}{2} \right)^2 N_1 N_2 \sqrt{\bar{c}_1^2 + \bar{c}_2^2} = 2N_1 N_2 \left(\frac{d_1 + d_2}{2} \right)^2 \sqrt{2\pi RT} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}, \dots(7)$$

where d_1, d_2 are the diameters, N_1 and N_2 the numbers per cm.³, \bar{c}_1, \bar{c}_2 the average velocities at the given temperature, and M_1 and M_2 the molecular weights.

TABLE OF MOLECULAR MAGNITUDES

Number of molecules per ml. of gas at S.T.P. = $N = 2.69 \times 10^{19}$.

Number of molecules per gram-molecule (22.415 litres in ideal state at S.T.P.) = $N = 6.03 \times 10^{23}$.

Mass of hydrogen atom = 1.69×10^{-24} gm.

Average velocity of hydrogen molecule at 0° = 1693 m./sec.

Translational kinetic energy of a molecule at 0° = 5.66×10^{-14} erg.

Rate of change of translational kinetic energy per 1° = 2.056×10^{-16} erg/degree.

Diameter of hydrogen molecule = 2.4×10^{-8} cm.

Mean free path of hydrogen molecules at S.T.P. = 1.22×10^{-8} cm.

Average distance apart of gas molecules at S.T.P. = 3×10^{-7} cm.

Number of collisions per second of oxygen molecules per cm.³ at S.T.P. = 5.85×10^{28} .

Time of describing free path of oxygen molecules at S.T.P. = 2.3×10^{-10} sec.

Shapes of molecules.—The molecular diameter is calculated in various ways, e.g. from the viscosity of the gas. It is usually assumed that the molecule is spherical, and although this is roughly correct for diatomic

molecules it does not hold for rod-shaped molecules, such as carbon dioxide and nitrous oxide, for which a single "diameter" can have little meaning. Attempts have been made to determine the distances between the atomic centres in such molecules, and these give a better picture of the shape of the molecule than a fictitious diameter.

The following table contains the values of molecular diameters in Å. (10^{-8} cm.) on the assumption of spherical molecules, as calculated from the viscosities.

He	1.18	H ₂	2.72	N ₂ O	4.66
Ne	2.60	O ₂	3.62	NO	3.76
A	3.66	N ₂	3.78	H ₂ O	4.66
Kr	4.16	CO	3.78	Cl ₂	5.40
Xe	4.92	CO ₂	4.66	H ₂ S	4.64

The distances between the lines in band spectra depend on the moments of inertia of the molecules, hence the distances between the atoms may be calculated from them. In this and other ways it is found that in the gaseous and solid states the CO₂ and N₂O molecules are rod-shaped. The H₂O molecule is a triangle with O at the apex; the NH₃ molecule is a flat tetrahedron with N at one apex and H at each of the other three. Methane CH₄ is a regular tetrahedron with the carbon atom inside.

Avogadro's number.—Important constants in the kinetic theory are: N = the number of molecules per ml. at S.T.P., and $\mathbf{N} = 22415 \times N$ = the number of molecules in a gram-molecule, which is the same for all gases and is called Avogadro's number. The value of \mathbf{N} has been determined by several methods, with an accuracy of about 1 per cent.

Determinations of \mathbf{N} have been made from experiments in radioactivity, from experiments on colloidal solutions (p. 257), on the electronic charge (p. 226), on the spectrum, the radiation of heat, the formation of clouds, and the blue colour of the sky. The numbers obtained are in excellent agreement, and point to the real existence of molecules. The best value of Avogadro's number is probably $\mathbf{N} = 6.03 \times 10^{23}$.



FIG. 73 — Spinthariscopes.

VALUES OF AVOGADRO'S NUMBER, \mathbf{N}

Classical kinetic theory	-	-	-	$6 \cdot 10^{23}$ (approximately)
Cloud formation	-	-	-	$8.3 \cdot 10^{23}$
Brownian movement	-	-	-	$6.09 \cdot 10^{23}$
Radiant heat	-	-	-	$6.03 \cdot 10^{23}$
Counting α -particles	-	-	-	$6.05-6.14 \cdot 10^{23}$
Electronic charge	-	-	-	$6.03 \cdot 10^{23}$

(1) The element radium emits atoms of helium called α -rays, with speeds of about 2×10^9 cm. per sec. (*i.e.* about 100,000 times faster than gas molecules) and large kinetic energy. When α -rays from a particle of radium *A* impinge on a screen of zinc-blende *B* in the spinthariscopes of Crookes (Fig. 73) each α -particle causes a flash of light visible under a lens *C*. It was

possible to count the α -rays emitted in a given time, and by collecting the helium from a large amount of radium over a long period, to show that the volume of helium produced from 1 gm. of radium was 0.46 mm.^3 per 24 hours. By comparing this with the counted number of α -particles (helium atoms) from a known weight of radium in a given time, the number of molecules (atoms) per ml. of helium at S.T.P., i.e. N , was found to be 2.7×10^{19} . Thence $22415 \times N - N = 6.05 \times 10^{23}$.

‡(2) A second method used by Rutherford and Geiger (1908), depends on the capacity of α -particles of making a gas through which they pass a conductor of electricity. A long glass tube AA' (450 cm. long and 2.5 cm. wide) (Fig. 74) was exhausted, and at the end A was placed a preparation

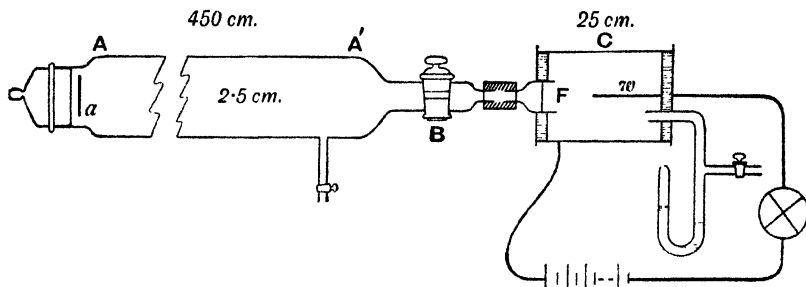


FIG. 74. - Rutherford and Geiger's apparatus.

of radium on a lead plate a , which expelled α -particles. Some of these passed along the tube and through the narrow tube B into the brass ionisation chamber C , where gas at low pressure was rendered conducting. A mica window F shut off gas from the exhausted tube AA' . Running axially through C and insulated from it by ebonite ends was a metal wire w , which was connected through a battery and electrometer to the outer surface of the brass vessel. As each α -particle entered the ionisation chamber (at the rate of about one a second), it made the gas conducting and the electrometer gave a deflection. In this way the individual α -rays were counted, and the value $N = 6.14 \times 10^{23}$ was found.

The specific heats of a gas.—When 1 gm. mol. of a gas is heated at constant volume from T° to $(T + 1)^\circ$ abs., the heat absorbed is called the **molecular heat at constant volume**, $C'_v = Mc_v$, where M = molecular weight, c_v = specific heat at constant volume. When the gas is heated at a constant pressure of 1 atm. it expands, doing work against the atmospheric pressure, and the heat absorbed is called the **molecular heat at constant pressure**, $C'_p = Mc_p$, where c_p = specific heat at constant pressure.

If the gas is ideal, no heat absorption results from the change of volume alone (cf. p. 118), and the difference of molecular heats ($C'_p - C'_v$) will be equal to the external work done, viz. (pressure) \times (increase of volume):

$$C'_p - C'_v = p(V' - V) = pV \left(\frac{T' + 1}{T} - 1 \right) = \frac{pV}{T} = R.$$

In a *monatomic gas* the heat absorbed increases only the kinetic energy of translation of the molecules, and for 1° rise of temperature this will be (p. 122) :

$$\frac{1}{T} \left(\frac{Mc^2}{2} \right) = \frac{3}{2}R = 2.982 \text{ g. cal.}$$

Hence $C_v = 2.982$ g. cal., $C_p = C_v + R = 4.970$ g. cal., hence for a monatomic gas

$$C_p/C_v = c_p/c_v = \gamma = 4.970/2.982 = 1.667. \quad \S$$

If the gas molecule contains more than one atom, part of the heat supplied at constant volume is used up in increasing the kinetic energy of rotation of the molecule : in addition, the energy of vibration of the atoms may be increased if the molecule is not rigid. If this total extra energy per 1° rise of temperature is denoted by E :

$$C_p/C_v = \frac{\frac{3}{2}R + R + E}{\frac{3}{2}R} < \frac{\frac{3}{2}R + R}{\frac{3}{2}R} < 1.667.$$

The value of C_p/C_v for a gas, the molecules of which contain more than one atom, is less than 1.667, as the table below shows.

Gas.	For-	C_p/C_v	Gas.	For-	C_p/C_v
	mula.	at 15°		mula.	at 15°
Helium - - -	He	1.667	Carbon dioxide -	CO ₂	1.302
Oxygen - - -	O ₂	1.396	Nitrous oxide -	N ₂ O	1.300
Nitrogen - - -	N ₂	1.405	Ammonia - - -	NH ₃	1.310
Air - - -	4N ₂ + O ₂	1.403	Sulphur dioxide -	SO ₂	1.285
Hydrogen - - -	H ₂	1.411	Hydrogen sulphide-	H ₂ S	1.340
Carbon monoxide -	CO	1.404	Methane - - -	CH ₄	1.310
Hydrogen chloride -	HCl	1.400	Ethylene - - -	C ₂ H ₄	1.250
Chlorine - - -	Cl ₂	1.355	Steam - - -	H ₂ O	1.306 (100°)

Even gases containing the same number of atoms in the molecule (O₂, Cl₂; SO₂, H₂S) have different values of γ ; the lower values indicate additional rotations or vibrations in the molecules.

The value 1.667 was found for mercury vapour by Kundt and Warburg (1876) and thus the monatomic character of the mercury molecule was confirmed. The method was used by Ramsay to show that argon and other inert gases are monatomic.

The value of γ is usually determined by methods depending on the formula for the velocity of sound :

$$u = \sqrt{\gamma p} D = \sqrt{\gamma RT/\bar{M}} \text{ for an ideal gas,}$$

or depending on the formula for *adiabatic expansion* :

$$p v^\gamma = \text{const.}, \text{ or } p T^{\frac{\gamma}{\gamma-1}} = \text{const.}$$

The specific heats of diatomic gases give values for the moments of inertia Σmr^2 of the molecules and hence of r , the distance between the atoms.

At low temperatures the rotational energy of hydrogen falls off, and at about -230° C. becomes zero. The molecular heat is then $C_v = 2.982$, the same as that for a *monatomic gas*. This is explained by the hypothesis that

the energy of rotation (and also of vibration of the atoms, if this form of energy is present) follows the quantum theory (p. 346), and decreases with temperature more rapidly at low temperatures than the value $\frac{1}{2}RT$, the classical expression for the energy of each degree of freedom of rotation, or RT for each vibration. The rotational effect is measurable only with hydrogen and deuterium, but a decrease is found for the vibrational energy of other gases.

Molecular attraction.—It has so far been assumed that the forces exerted by gas molecules on one another are negligibly small. This is only approximately true. Gases are usually more compressible than the ideal gas obeying Boyle's law, and this may be explained by assuming that the molecules attract one another, the attraction becoming greater the closer the molecules come together. When the gas is liquefied the molecular attraction is sufficient to prevent the spontaneous separation of the molecules in an open vessel. A liquid is much less compressible than a gas, and the compressibility of a gas falls off considerably at high pressures. This effect is assumed to be due to the space x occupied by the molecules, and if this is comparable with the total space v , only the intermolecular space $(v - x)$ is available for compression.

These two factors are taken into account by the equation of van der Waals, which replaces the ideal gas equation $p v = RT$ by :

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where a and b are constants. The term a/v^2 is the molecular attraction correction, which is inversely proportional to the square of the volume and adds itself to the external pressure p ; b is the correction for the space occupied by the molecules. According to van der Waals, b is equal to four times the total volume actually occupied by the molecules, but it appears to be $4\sqrt{2}$ times the latter. This equation gives good results with some gases (e.g. ethylene), but the attraction term depends on the temperature.

Liquefaction of gases.—Ammonia gas was liquefied by compression by Van Marum, and in 1799 by cooling, by Guyton de Morveau. Sul-

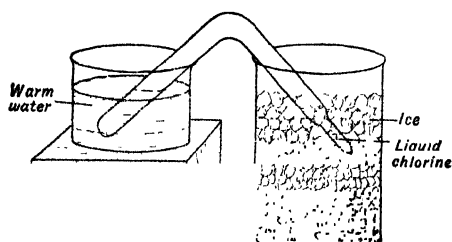


FIG. 75.—Liquefaction of chlorine by Faraday.

phur dioxide was liquefied by cooling by Monge and Clouet: in 1806 chlorine was liquefied by compression by Northmore. In 1823 liquid chlorine was again obtained by Faraday, by warming chlorine hydrate in one limb of a sealed U-tube, the other limb of which was cooled in a freezing mixture (Fig. 75).

In later experiments, Faraday was able to liquefy hydrogen sulphide, hydrogen chloride, carbon dioxide, nitrous oxide, cyanogen, and ammonia; but oxygen, nitrogen, and hydrogen resisted all attempts to reduce them to the liquid state, and hence they were called *permanent gases*.

Most of the attempts relied on the application of pressure to the gases. Some gases may be liquefied by pressure without very strong cooling; the pressures in atm. required to liquefy the gases at 0° are:

Sulphur dioxide	1.53	Ammonia	- - 4.26
Chlorine - - -	3.66	Carbon dioxide	- 34.55

Pressures up to 2000 atm. were tried without result by Natterer (1844) with nitrogen, oxygen, and hydrogen.

In 1869 Andrews discovered that a gas cannot be liquefied by any pressure, however high, unless it is cooled below what is called the **critical temperature** of the gas. Just below this temperature the gas is liquefied by the application of the **critical pressure**. The volume occupied by 1 gm. of a substance at the critical temperature and under the critical pressure is the **critical volume**.

At the critical point liquid and vapour become identical, and it is possible to convert gas *continuously* into liquid without any separation into liquid and vapour phases. Cagniard de la Tour in 1822 had shown that when a liquid such as ether is heated in a sealed tube, the liquid meniscus vanishes at a certain temperature and reappears at this temperature on cooling.

The critical temperatures of the so-called permanent gases lie below the lowest temperatures attained by older experimenters. When it was clear that strong cooling was necessary and that high pressures alone could never succeed in the case of these gases, the problem was solved, independently, by Pictet and Cailletet in 1877.

Pictet's method.—Pictet used the apparatus shown in Fig. 76. Oxygen generated in the retort *P* by heating potassium chlorate, was compressed by its formation in a copper tube, cooled in liquid carbon dioxide *L* boiling under reduced pressure, and fitted with a pressure gauge *Q* and release valve *N*. The carbon dioxide was reliquefied by a pump *G* in a second copper tube; *EF*, surrounded by liquid sulphur dioxide boiling under reduced pressure, and circulated by a second pump.

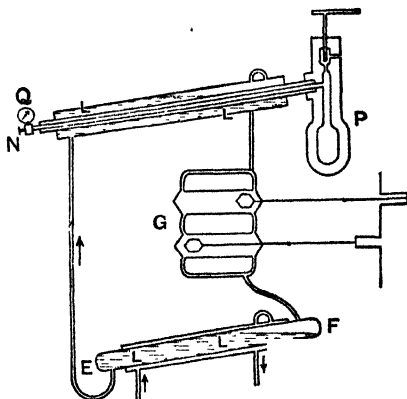


FIG. 76.—Liquefaction of oxygen by Pictet.

Pictet reduced the temperature to -140° , and the pressure rose to several hundred atmospheres. On opening the release-valve *N*, a jet of liquid oxygen issued from it, at once boiling away.

Cailletet's method.—Cailletet compressed the gas by a powerful pump forcing water into a strong steel vessel *B*, Fig. 77, in which the gas was contained in a tube *T*, sealed below by mercury. Water forced into *B* drove the mercury into *T* and strongly compressed the gas. The pressure was then suddenly released by opening a valve which allowed

the water to escape, and the gas expanded suddenly and hence without appreciable exchange of heat with the surroundings (*adiabatic expansion*).

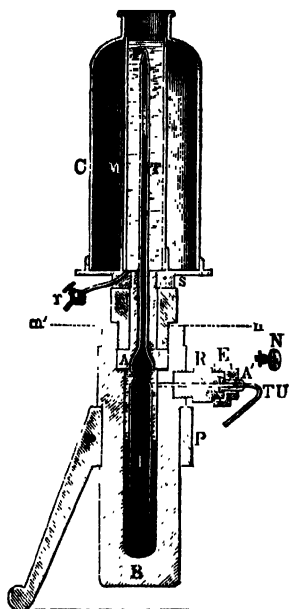


FIG. 77.—Liquefaction of gases by Cailletet.

work done by a gas in adiabatic expansion. If a given mass of gas, of volume v_1 (Fig. 78), is forced under a pressure p_1 through the plug into a space under a lower pressure p_2 (say $\frac{1}{2}p_1$), it occupies a larger volume v_2 . The work done on the gas is p_1v_1 , that done by the gas is p_2v_2 . If the gas obeyed Boyle's law, $p_1v_1 = p_2v_2$ ($v_2 = 2v_1$; $p_1 = 2p_2$), and no external work would be done; if no other effect were involved there would be no change of temperature. Since v_2 is greater than v_1 , the molecules of the gas have separated, and since there is a slight attraction between them, *internal work* has been spent in separating them. The energy required for this *internal work* is taken from the gas, and a slight cooling results. Usually, both external and internal work are involved; p_2v_2 is slightly larger than p_1v_1 , since the gas is usually slightly more compressible than an ideal gas, and p_1 is greater than p_2 . A little heat is absorbed in providing this extra work $p_2v_2 - p_1v_1$, but much more is absorbed to supply the internal work.

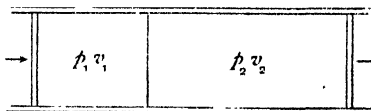


FIG. 78.—Diagram illustrating free expansion of gases.

The work done by the gas against the external pressure in expanding adiabatically is provided by the energy of the gas, and the decrease of the kinetic energy of the gas molecules causes a fall in temperature. In Cailletet's experiment the temperature fell to the point of liquefaction of the oxygen. A fog of liquid droplets was seen momentarily in the tube, at once vanishing as heat was communicated from the walls.

Joule-Thomson effect.—The liquefaction of air in bulk was effected in 1895, independently, by Hampson in England and by Linde in Germany, by the use of a new principle, viz. the *Joule-Thomson effect*, investigated by Joule and William Thomson (later Lord Kelvin) from 1852 to 1862. When a compressed gas escapes into the free air through a plug of silk in a boxwood tube, a slight cooling effect occurs with most gases (air, oxygen, nitrogen, carbon dioxide), but with hydrogen there is a slight heating effect.

This temperature change is quite different from that due to the external

Liquefaction of air.—In the case of air the Joule-Thomson cooling effect in degrees C. is given by

$$\frac{\text{difference of pressures in atm.}}{4} \times \left(\frac{273}{T_1}\right)^2,$$

where T_1 is the absolute temperature of the air before expansion.

If air at 0° C., and under a pressure of 100 atm., is expanded through a valve to atmospheric pressure, the fall of temperature will be $(99/4) \times (273/273)^2 = 24.7^\circ$. If this cool air sweeps over the surface of a copper pipe, bringing compressed air to the valve (Fig. 79), the expanded air takes heat from the air coming to the valve, becoming itself warmed nearly to the atmospheric temperature. The cooled compressed air after expansion becomes 30.3° colder, as the above formula shows, and this cold air sweeps over the inner tube, further reducing the temperature of the compressed air coming down. The cooling effect *accumulates*, and the air issuing from the nozzle finally becomes so cold that it liquefies.



FIG. 79.—Cooling of gases by free expansion

A diagram of an air liquefaction apparatus is given in Fig. 80. Air is drawn through purifiers to remove carbon dioxide and then compressed. The heat of compression is taken out by a cooler and the air passes through an apparatus in which moisture is removed. The compressed air then expands through a jet and in so doing becomes cooled. The cold air sweeps over the outside of a spiral metal pipe bringing

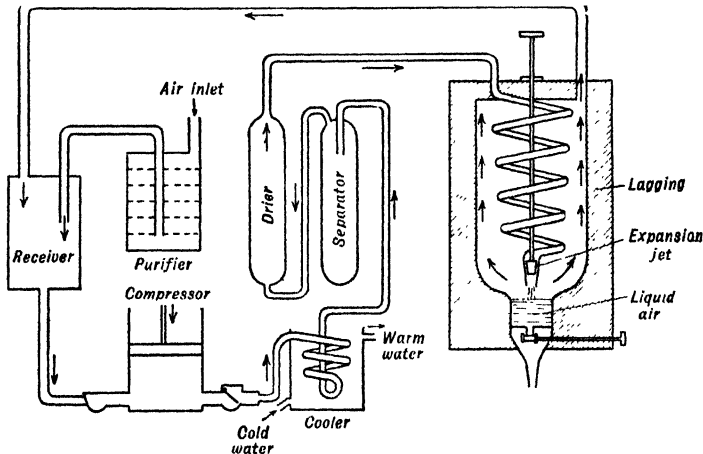


FIG. 80.—Production of liquid air.

the compressed air to the jet, and so cools the compressed air before expansion. This cooling effect accumulates and finally the air becomes

so cold that it liquefies on leaving the jet. Liquid air as obtained from the liquefier is richer in oxygen than gaseous air. Usually it contains from 50 to 60 per cent by weight of oxygen as compared with 23 in gaseous air.

Liquid air is kept in double-walled glass Dewar ("thermos") flasks (Fig. 81), the inner surfaces of which, silvered to reflect heat, have a high vacuum between them to cut down heat transmission to a minimum.

Liquid air and liquid oxygen are stored in spherical metal vacuum vessels holding 5-30 galls., the inner vessel being suspended by a thin metallic neck and the annular space exhausted. A high vacuum is maintained by means of a tube of absorbent charcoal open at the end exposed to the vacuous space and with the other (closed) end immersed in the liquid air or oxygen. The daily loss is not more than 5 per cent.

Liquid air is usually slightly turbid, because it contains particles of ice and solid carbon dioxide. If filtered through a large filter paper it is a clear liquid with a pale blue colour, due to liquid oxygen. If poured out into the air it evaporates, producing thick white clouds of condensed moisture. Its temperature is about -190° , and when exposed to this extreme cold many substances undergo remarkable changes in properties. Lead becomes elastic, and rubber hard and brittle. Mercury is frozen to a malleable solid. Raw meat, fruits, flowers, etc., become hard, and can be powdered in a mortar. A kettle containing liquid air "boils" briskly on a slab of ice, and copious clouds of "steam" (*i.e.* atmospheric moisture condensed to particles of ice by the cold of the escaping evaporated air) are emitted from the spout. The phosphorescence of calcium sulphide is quenched at the temperature of liquid air, but appears again on warming. Sulphur and mercuric iodide become much paler in colour on cooling in the liquid.

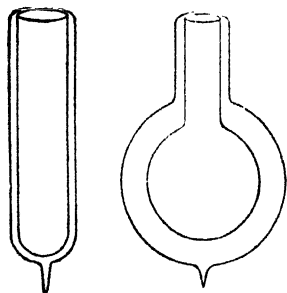


FIG. 81.—Vacuum vessels

Critical constants from van der Waals's equation.—Van der Waals's equation

$$(p + a/V^2)(V - b) = RT,$$

when multiplied out is a cubic equation in the volume V :

$$V^3 - V^2 \left(b + \frac{RT}{p} \right) + V \frac{a}{p} - \frac{ab}{p} = 0. \dots\dots\dots(1)$$

If the three roots are x_1, x_2, x_3 , then

$$(V - x_1)(V - x_2)(V - x_3) = 0.$$

The three roots may all be real, or one may be real and the other two imaginary. Hence for every value of p and T there are one or three values of V . The first case corresponds with a real gas. At the critical

point the three roots become equal, and equal to the critical volume of 1 g. mol. : $x_1 = x_2 = x_3 = V_c$; hence

$$(V - V_c)^3 = V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0 \dots \dots \dots (2)$$

By comparing (1) and (2) and equating the coefficients of like powers of V it is found that

$$b + RT_c/p_c = 3V_c; \quad a/p_c = 3V_c^2; \quad ab/p_c = V_c^3$$

(since when $V = V_c$, the pressure and temperature are also the critical values). From these equations it is easily found that

$$V_c = 3b, \quad p_c = a/27b^2, \quad T_c = 8a/27bR. \dots \dots \dots (3)$$

Liquids.—The attractive forces exerted by molecules on one another in the liquid state are considerable. In a liquid the molecules are close together, so that there are practically no free paths.

Since the actual space occupied by spheres of radius r most densely packed is 0.74 of the total volume, if the molecules in a liquid are in contact,

$$\frac{4}{3}\pi r^3 N = 0.74V,$$

where N is Avogadro's number and V the molar volume (= mol. wt./density). This gives an *approximate* value of the molecular radius.

A molecule in the body of a liquid is attracted equally in all directions and the resultant force on it is zero. The range of attractive forces is small; van der Waals calculated an order of 10^{-6} cm. Molecules in the *surface* however, are subject to a resultant attraction due to the unbalanced forces of the molecules below them, and are under a pressure tending inwards (Fig. 82). This resultant force gives rise to **surface tension**.

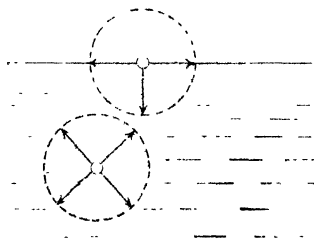


FIG. 82.—Diagram indicating the range of molecular forces in a liquid.

The attractive forces between molecules are not always uniform in all directions, but may proceed in one or two directions only, as if the molecules were small magnets. The molecules in the surface will then mostly be arranged with the same parts pointing in one direction. Investigations of Rayleigh (1899) indicated that the thinnest of oil films on water were unimolecular, and the formation of unimolecular films has been proved in many cases by Langmuir and Harkins (from 1917). A drop of a solution of an insoluble fatty acid (or other substance) in benzene is brought on a perfectly clean surface of water. The solvent evaporates, leaving an isolated patch of film. By bringing a strip of paraffined paper across the surface of the water so as to enclose the film and the sides of the trough, a resistance is encountered when the film just fills the area between the strip and the edges of the trough.

The area of the film is then equal to the area A between the strip and the

sides of the trough, and since the weight w of the film is known, the area a occupied by a single molecule in the unimolecular film is given by :

$$a = \frac{AM}{wN},$$

where M is the molecular weight of the substance in the film and N is Avogadro's number. The thickness t of the film can be calculated on the assumption that the density is the same as that of the substance in bulk, δ :

$$\delta = \frac{1}{t} \cdot w.$$

For fatty acids a is practically the same with varying lengths of chains of carbon atoms, so that it is assumed that the molecule is orientated vertically on the water surface with the carboxyl group (COOH) of the acid immersed in the water and the carbon chain outside.

Kinetic theory of evaporation.—Some molecules in a liquid have more than the average kinetic energy. Such molecules, on approaching the surface, have enough energy to break away from the attractive forces, and proceed outwards into the space above the liquid. This is the phenomenon of evaporation.

Escape of molecules of higher kinetic energy reduces the mean energy of the liquid, which becomes cooler. To keep the temperature constant, heat must be added from outside : this is the latent heat of evaporation.

Molecules in the vapour which approach the liquid are attracted near the surface, describe curved orbits, and may be caught by the surface and dragged into the liquid. They are accelerated in the field of attraction, and pass into the liquid with increased kinetic energy. Heat is therefore given out on condensation. Eventually, as many molecules leave the liquid as pass back again per second ; this is a condition corresponding with the saturation vapour pressure and is a *kinetic equilibrium*, due to two opposite processes going on at equal rates.

If the forces acting on liquid molecules are as shown in Fig. 82, the work done in bringing a molecule from inside the liquid to the surface will be half that required to remove it altogether from the liquid to the vapour space, the latter being measured by the latent heat of evaporation (Stefan, 1886). The translational kinetic energy of the molecule is the same in the liquid and vapour, since it depends only on the temperature.

Molecular weights of liquids.—If the particles in a liquid move about as individuals, they have definite molecular weights. Molecules of more than one kind may be present. When the liquid molecule is the same as the gas molecule, the liquid is called a *normal liquid*. If it contains molecules formed by the association of simple molecules, it is called an *associated liquid*.

Attempts have been made to find the molecular weights of liquids by measurements of surface tension. The product $\sigma [V]^{\frac{2}{3}}$ where σ = surface tension in dynes per cm., V = molecular volume = M/D (D = density) in ml., is proportional to the surface energy of 1 mol of liquid in the form of a sphere, and was called by Fötvös, and by Ramsay and Shields, the *molecular surface energy*. This decreases with temperature t° C. according to the equation :

$$\sigma [V]^{\frac{2}{3}} = k(t_c - t - \theta),$$

where k is a constant and t_c is the critical temperature. For most liquids k is approximately 2.12, but in some cases, as with water, alcohol and acetic acid, it is smaller.

For bromine, $\sigma = 44$ at 13° C., $t_c = 302.2$; $M = 160(\text{Br}_2)$, $D = 3.12$;

$$\therefore k = 44 \left(\frac{160}{3.12} \right)^{\frac{2}{3}} \cdot (302.2 - 13 - 6) = 2.145.$$

Since this is nearly 2.12, bromine is assumed to be normal.

For water, $\sigma = 73$ at 15° C., $t_c = 370$, $M = 18$, $D = 1$, hence

$$k = 73 \cdot (18)^{\frac{2}{3}} \cdot (370 - 15 - 6) = 1.497.$$

This is smaller than the normal value, and water is assumed to be associated. If the molecular weight of water is assumed to be $x \cdot 18$, where $x =$ degree of association, we may expect to get the normal value of k (since $18x$ is the true molecular weight), hence by division:

$$i^{\frac{2}{3}} = 2.12 \cdot 1.497; \therefore x = 1.69.$$

In some cases (*e.g.* fused metals) the method leads to values of x smaller than 1 which are difficult to interpret, and the calculation of degrees of association, as above, is now regarded as of doubtful validity.

Another indication of association is the value of the Trouton coefficient, Ml_p/T_0 , where l_p is the latent heat of evaporation per gm., and T_0 the boiling point abs. For normal liquids this is about 21, for associated liquids it is larger, *e.g.* 26.9 for alcohol and 25.9 for water.

The Parachor.—For a non-associated liquid the influence of temperature on the surface tension σ is given by the relation $M\sigma^{1/4}/(D \cdot d) = \text{const.} = [P]$, where D and d are the densities of liquid and vapour and $M =$ mol. wt. In many cases d can be neglected. $[P]$ is called by Sugden the *parachor*, and is interpreted as the molecular volume at a standard internal pressure. The parachor is very nearly additively composed of a sum of terms for the separate atoms together with constants for the particular forms of linkages. Double bonds, rings, etc., have characteristic values, so that the parachor has been used to determine the constitution of molecules.

Solids.—In the solid state it is assumed that each molecule performs oscillations of small amplitude about its fixed position of equilibrium. When heat is imparted to the solid, the amplitudes of the oscillations increase, and at a certain temperature the molecules collide with each other and break loose. This is the point of fusion. The molecules in a solid exert large attractive forces on each other and in separating them work is done, which is equivalent to the latent heat of fusion. Since the solid is only slightly compressible, there must be repulsive forces between the molecules which increase more rapidly than the attractive forces at small distances between the molecules. In the ordinary state, these two sets of forces are in equilibrium. In some cases the particles in a solid are rotating (or at least swinging to and fro around an axis), as well as oscillating about fixed positions.

The process of building a solid structure from a liquid takes place round definite nuclei. Small crystal aggregates are formed at a small number of points, and radiating masses of crystals shoot out from these centres until the whole is solid. Crystallisation does not usually begin at the freezing point unless solid is present, but the liquid must be *super-cooled*. A solid, on the other hand, always fuses as soon as the melting point is reached, and cannot be permanently superheated. At the melting point, when solid and liquid are present, there is a condition of kinetic equilibrium. The solid state is not adequately described by the kinetic theory used for gases, but requires the quantum theory (see Chapter XXI).

The molecular weight of a solid has little or no significance, since the particles composing the crystal may not correspond with the molecular formula of the substance. In sodium chloride crystals, the individual particles are electrically charged sodium and chlorine ions, Na^+ and Cl^- , not molecules of NaCl , and a diamond crystal consists of single atoms of carbon linked by strong forces to which the hardness and low volatility are due. The idea that a solid has a high molecular weight, so that the molecules in diamond are C_n , for example, is incorrect. In crystals of organic compounds the individual molecules, such as C_{10}H_8 in naphthalene, are present, but in salts the crystals are usually lattices of separate ions.

Solutions.—When a gas is brought in contact with a liquid, solution occurs until the concentration of dissolved gas is in a fixed ratio to that in the gas-space, as required by Henry's law (p. 64). A state of kinetic equilibrium is set up with equal numbers of gas molecules entering and leaving the liquid in unit time.

The mass of gas impinging on the liquid surface per second is $\frac{1}{2}D\bar{u}$ (p. 120) = $\frac{1}{2}D \times \frac{1}{2}\bar{c} = D\sqrt{\bar{c}^2}/\sqrt{6\pi} = 0.230D\sqrt{\bar{c}^2}$. In oxygen at S.T.P., $D = 0.001429$ gm. per ml., $\sqrt{\bar{c}^2} = 4.61 \times 10^4$ cm. per sec., \therefore the mass of oxygen striking 1 sq. cm. of the liquid surface per second is $0.230 \times 0.001429 \times 4.61 \times 10^4$ gm. = 15.1 gm. This contains 2.85×10^{23} molecules, or the number in about 10 litres.

Some of the impinging gas molecules pass through the surface into the liquid, owing to molecular attraction. Some gas molecules moving in the liquid approach the surface, and if the kinetic energy of these is much above the average value, they will pass into the gas-space. This occurs the oftener the more gas molecules are dissolved. A state of equilibrium is reached when as many molecules enter as leave the liquid per second.

When the pressure of the gas is raised, the number of molecules per unit volume increases, and the number striking the surface becomes larger in the same ratio. The number of molecules per unit volume in the liquid also increases. Hence more molecules leave it than previously. When there is equilibrium, the same number leave as enter per second, but if the number entering is increased n times the number in unit volume of liquid also increases n times. This is Henry's law.

If we imagine people walking into a room through one door and out

through another, so that as many enter as leave, then if they enter twice as often there will be double the number in the room, although they are also leaving it at twice the previous rate.

When a solid dissolves in a liquid, molecules pass from their centres of oscillation on the surface of the solid, and in a saturated solution molecules are caught into positions of oscillation. An irregular or broken crystal suspended in a saturated solution tends to become more perfect in shape, one part dissolving and being deposited in another place. Ultramicroscopic experiments (Traube and von Behren, 1928) show that a crystal in dissolving is often broken up into small aggregates of molecules (*submicrons*), which, after a very short interval, disperse as molecules or ions. In forming crystals the reverse process occurs, strings of submicrons building up small "blocks" of the crystal aggregate.

Attempts have been made to find the radii of particles in solutions by assuming them to be spheres and applying Stokes's law (p. 6) :

$$v = 1.6\pi\eta r,$$

where v is the mobility (= speed under unit force on the particle) and η the viscosity of the liquid. The force may be an osmotic pressure gradient as in diffusion, or an electric potential gradient as in the case of a migrating ion, or both combined as in the diffusion of ions. This method gives good results only with large (colloidal) particles.

CHAPTER XI

OXYGEN AND OZONE

History.—Oxygen was first isolated by Scheele in 1772 and was discovered independently by Priestley in 1774 (p. 30). Its elementary nature was recognised by Lavoisier (p. 33).

Occurrence.—Oxygen occurs in the free state as a gas of the molecular formula O_2 , to the extent of 21 per cent by volume or 23 per cent by weight in the atmosphere, and takes part in processes of combustion; its biological functions in respiration make it important. The gas is sparingly soluble in water, but the small quantity dissolved is essential to the life of fish.

Combined oxygen occurs in water, in vegetable and animal tissues, in nearly all rocks and in many minerals: it occurs to a larger extent (about 50 per cent) in the earth's crust than any other element.

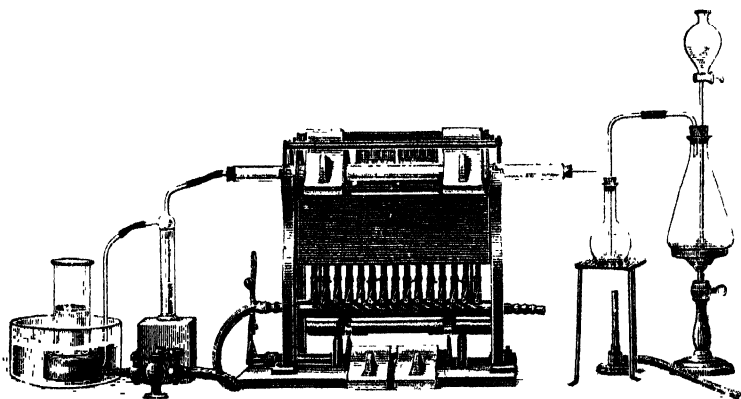
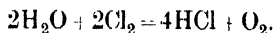


FIG. 83. —Decomposition of steam by chlorine.

Preparation from water.—Oxygen is obtained from water by passing a mixture of steam and chlorine through a strongly heated silica tube containing pieces of broken porcelain:

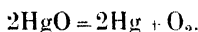


The hydrogen chloride is removed by a wash-bottle containing sodium hydroxide solution and the oxygen collected over water (Fig. 83).

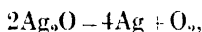
Oxygen is evolved at the positive electrode in the electrolysis of acidulated water (p. 40): $2H_2O = 2H_2 + O_2$.

A solution of barium hydroxide with nickel electrodes may also be used, but on prolonged electrolysis an explosive mixture of oxygen and hydrogen may be evolved at the positive electrode.

Preparation of oxygen from oxides.—Oxygen may be obtained by heating some metallic oxides. Mercuric oxide strongly heated in a hard glass tube decomposes; globules of mercury collect in the cooler parts of the tube and oxygen gas is evolved; if collected over mercury it is pure and dry:

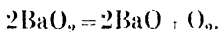


Silver oxide decomposes at a lower temperature than mercuric oxide:



and when prepared by precipitation of silver nitrate solution by pure potassium hydroxide solution in absence of atmospheric carbon dioxide, the silver oxide gives very pure oxygen.

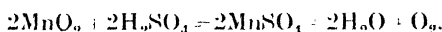
Higher oxides of metals decompose on heating into oxygen and lower oxides. Barium peroxide decomposes into oxygen and barium monoxide (baryta):



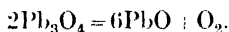
Black manganese dioxide decomposes at a *bright-red* heat, giving off oxygen and leaving a brownish-red lower oxide, trimanganic tetroxide Mn_3O_4 :



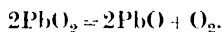
Manganese dioxide evolves oxygen more readily when heated with concentrated sulphuric acid:



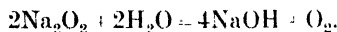
Red lead Pb_3O_4 on heating evolves oxygen and leaves yellow lead monoxide PbO :



Lead dioxide PbO_2 , a plum-coloured powder, evolves oxygen on heating and leaves lead monoxide PbO :

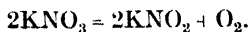


Oxygen is evolved by dropping water on sodium peroxide Na_2O_2 , but this experiment may result in an explosion since some metallic sodium may be present in the peroxide



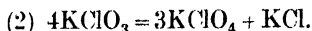
Preparation of oxygen from salts.—Some salts containing oxygen evolve oxygen gas on heating.

Nitre or saltpetre, potassium nitrate KNO_3 , on heating melts and at a rather high temperature gives off bubbles of oxygen, leaving potassium nitrite KNO_2 , which solidifies on cooling:



Potassium chlorate crystals heated in a hard glass tube melt at 360° and then evolve oxygen: (1) $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$.

As the reaction proceeds the evolution of gas slackens and the salt becomes pasty, finally almost solid, and at this stage the residue contains potassium chloride and potassium perchlorate KClO_4 :

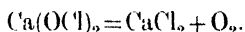


If the temperature is raised the mass fuses again, oxygen is evolved and finally solid potassium chloride remains:



Reactions (1) and (2) proceed *independently* from the commencement and equations showing the simultaneous formation of oxygen, chloride and perchlorate in a definite ratio are regarded as inaccurate. The oxygen obtained from chlorate may contain a little chlorine, which is removed by washing with sodium hydroxide solution.

A solution or paste of bleaching powder heated with a few drops of cobalt chloride solution evolves oxygen. The bleaching powder solution contains calcium hypochlorite Ca(OCl)_2 . This precipitates from a cobalt salt solution a black higher oxide of cobalt, Co_2O_3 or CoO_2 , in presence of which the calcium hypochlorite is rapidly decomposed with the formation of calcium chloride and evolution of oxygen:



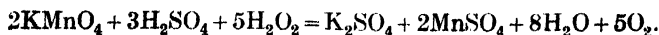
The cobalt oxide appears to undergo no change, but probably undergoes alternating oxidation and reduction, acting as a catalyst (p. 142).

Potassium permanganate KMnO_4 , which forms purple (almost black) crystals, on heating at 240° evolves pure oxygen without fusing, the crystals falling to a black powder of a mixture of potassium manganate K_2MnO_4 and manganese dioxide:



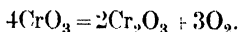
If the cooled black residue is thrown into a large beaker of water, the potassium manganate dissolves to a *green* solution which almost immediately becomes *pink* from the conversion of the manganate into permanganate by the action of the carbon dioxide dissolved in the water. By adding a little sodium hydroxide solution (which combines with the carbon dioxide) to the water before the experiment, the green colour remains but becomes pink on adding dilute sulphuric acid.

Potassium permanganate explodes violently when heated with concentrated sulphuric acid, but when hydrogen peroxide solution is mixed with a solution of the permanganate and diluted sulphuric acid, the two compounds decompose each other, forming a nearly colourless solution, and oxygen is evolved:

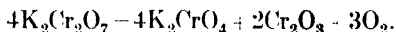


A solution of 5 gm. of KMnO_4 in a cooled mixture of 100 ml. of water and 50 ml. of concentrated sulphuric acid is dropped from a tap-funnel into 100 ml. of 20-volumes hydrogen peroxide in a flask. The oxygen evolved is collected over water.

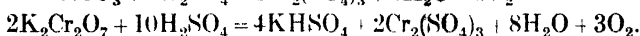
Chromium trioxide CrO_3 , which forms red crystals, melts on heating and at about 420° evolves oxygen, leaving a green residue of chromic oxide (a little chromium trioxide sublimes) :



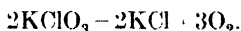
Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$, which forms bright-red crystals, melts on heating and when *strongly* heated evolves oxygen, leaving a mixture of yellow potassium chromate K_2CrO_4 , soluble in water, and green chromic oxide Cr_2O_3 , insoluble in water :



Chromium trioxide and potassium dichromate evolve oxygen when heated with concentrated sulphuric acid, chromic sulphate being formed :*



Laboratory preparation of oxygen.—Potassium chlorate decomposes at a much lower temperature if previously mixed with manganese dioxide. Only the chlorate is decomposed, and in this case no perchlorate is formed :



This reaction is generally used in the laboratory for the preparation of oxygen.†

A mixture of 25 gm. of potassium chlorate with 5 gm. of manganese dioxide (*oxygen mixture*) evolves oxygen freely when heated in a glass tube at a temperature below the melting point of the chlorate. The heating must be carefully regulated, as the decomposition of potassium chlorate, unlike that of mercuric oxide, *evolves* heat and under certain conditions may become explosive.

The oxygen mixture is heated in a large test-tube clamped in a horizontal position and fitted with a fairly wide glass delivery tube passing through a cork in the test-tube and dipping at the other end under water in a pneumatic trough. Over this end is supported a glass cylinder full of water and standing on a beehive shelf in the trough (Fig. 84). The mixture is cautiously heated with a small flame, beginning at the end near the cork, and the flame is withdrawn from time to time

* The residue from potassium dichromate and sulphuric acid is practically insoluble in water.

† The student should remember that only some of the reactions of preparation of substances are normally used ; *pure* oxygen is best prepared by heating potassium permanganate or by the interaction of acidified permanganate solution and hydrogen peroxide. Oxygen may be *dried* by means of calcium chloride, concentrated sulphuric acid or phosphorus pentoxide, and must then be collected over mercury.

when the evolution of gas begins to be violent. The delivery tube must be taken out of the water before the test-tube is allowed to cool, since otherwise water will be forced back into the hot tube and crack it.

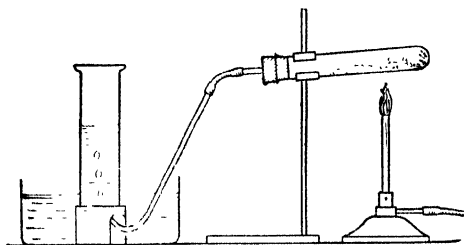


FIG. 84 — Preparation of oxygen

Warning.— Manganese dioxide adulterated with powdered coal or antimony sulphide explodes violently on heating with chlorate. Serious and even fatal accidents have been caused in this way, and a *little* of the mixture should always be heated in an open test-tube before beginning the experiment in order to be sure that no deflagration occurs.

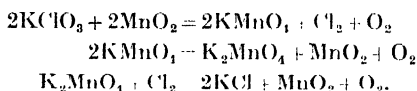
Catalysis.— The manganese dioxide in the oxygen mixture undergoes no *permanent chemical change* in the reaction and may be recovered by dissolving out the potassium chloride from the residue with water. Other oxides such as ferric oxide and cupric oxide act similarly, and are also left chemically unchanged after the reaction.

This action was discovered by Döbereiner in 1820 and is an example of what was called *contact action* by Mitscherlich in 1833 and *catalysis* by Berzelius in 1835.

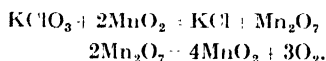
A catalyst is a substance which accelerates a chemical reaction without itself undergoing any permanent chemical change.

If several products are obtainable in a reaction, a catalyst may be able to direct the course of the reaction.

The catalytic action of manganese dioxide was explained by McLeod (1889) as due to a cycle of reactions :



Fowler and Grant (1890) supposed that a higher oxide of manganese is alternately formed and reduced :

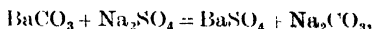


Fuse some potassium chlorate in two hard glass tubes. To one add a *very small* quantity of manganese dioxide (or better Mn_2O_4), to the other a *very small* quantity of chromic oxide Cr_2O_3 . Observe that (i) oxygen is evolved ; (ii) the fused salt becomes permanently pink (KMnO_4) and yellow (K_2CrO_4),

respectively. KMnO_4 cannot exist alone at the temperature of the fused chlorate, hence it must be continuously decomposed and reproduced by a cycle of reactions. A little ferric oxide Fe_2O_3 produces a violent effervescence, and on cooling the mass is slightly pink from the formation of potassium ferrate, K_2FeO_4 .

McLeod observed that pieces of manganese dioxide put into fused chlorate break up into a very fine powder. The *physical* state of the manganese dioxide changes, which suggests that it has entered into reaction and is reproduced.

It may be difficult to see how manganese dioxide can exert any action on *solid* chlorate, since the catalytic effect occurs below the fusion point of the latter. But some local fusion probably occurs on account of the heat evolved in the reaction (flashes of light are always seen), and in any case L. H. Parker (1914-18) has shown that chemical action may occur between solids. The reaction :



and the reverse reaction, take place to a limited extent when the dry powdered mixture is heated short of fusion, or simply triturated in a dry mortar. Reaction also occurs in the dry powder when it is strongly compressed, as was shown by Spring.

Physical properties of oxygen.—Oxygen is a colourless gas, without smell or taste. It is slightly heavier than air. It is sparingly soluble in water. Oxygen is difficult to liquefy, b.pt. -183.0° ; the liquid is pale blue in colour and is appreciably magnetic. At still lower temperatures light-blue solid oxygen is obtained, m.pt. -218.4° . It should be noted that solid oxygen cannot be obtained by rapid evaporation of the liquid (as can solid nitrogen); the liquid must be cooled in liquid hydrogen.

Combustion.—The combination of substances with oxygen, with the evolution of heat and light, is called combustion. Substances which burn in air burn with much greater brilliancy in pure oxygen, since the nitrogen in air acts as a diluent, absorbing part of the heat given off in combustion. Some substances, such as phosphorus, oxidise *slowly* when exposed to air without catching fire, because the heat produced by oxidation is dissipated too rapidly to raise the temperature to the ignition point.

Finely divided phosphorus, obtained by the evaporation of a solution of phosphorus in carbon disulphide poured on filter paper, takes fire spontaneously in air.

Finely divided lead, called pyrophoric lead (made by heating lead tartrate), glows in air and fumes of lead oxide are formed.

Precipitate a solution of lead acetate with a solution of tartaric acid. The white precipitate of lead tartrate, $\text{PbC}_4\text{H}_4\text{O}_6$, is filtered, washed, and dried in a steam-oven. Small portions are placed in narrow tubes, sealed at one end and drawn out at the other. The tartrate is heated until fumes

are no longer evolved, and the tubes are sealed. If a tube, after cooling, is cut with a file and the finely divided pyrophoric lead shaken out, the metal glows brightly, forming yellow fumes of lead oxide PbO .

Combustion of non-metals in oxygen.—Some non-metallic elements, such as phosphorus, sulphur, and carbon, burn in oxygen to form *acidic oxides*, i.e. oxides which form acids on solution in water (see p. 74). Hydrogen on combustion forms water, which is a *neutral oxide*, i.e. has no acidic or basic reaction.

In the combustion of solids such as phosphorus, sulphur and carbon in oxygen, the substance contained in the bowl of a *deflagrating spoon* is kindled and placed in a jar of oxygen (Fig. 85).

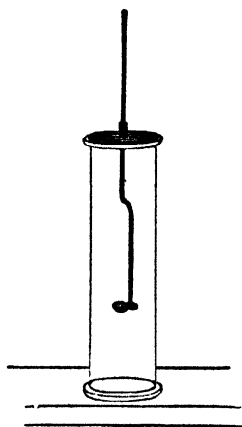
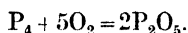
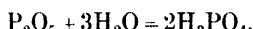


FIG. 85.—Gas jar and deflagrating spoon.

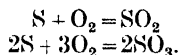
(1) White phosphorus is cut under water, a small piece rapidly dried by pressing between filter papers, and put in the spoon with dry crucible tongs. *The dry phosphorus must on no account be handled with the fingers as it may take fire.* The phosphorus is kindled by touching it with a hot wire and put into the jar, when it burns in the oxygen with an exceedingly brilliant white flame, producing a white cloud of phosphorus pentoxide which settles in flocks on the inside of the dry jar :



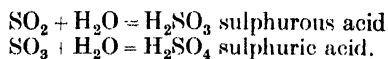
When water is poured into the jar the oxide dissolves and phosphoric acid H_3PO_4 is formed, which changes the colour of blue litmus solution to red :



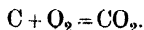
(2) A piece of roll sulphur when kindled in a spoon burns with a bright blue flame when introduced into a jar of oxygen. The gas sulphur dioxide SO_2 is the main product of the combustion, but a little solid sulphur trioxide SO_3 is also formed, which makes the gas slightly cloudy :



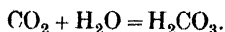
When shaken with water, the products of combustion dissolve, forming a solution which reddens litmus :



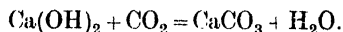
(3) A piece of wood charcoal strongly heated in a spoon burns brightly, often throwing off bright sparks, when placed in oxygen. Carbon dioxide CO_2 is the chief product of the reaction, although a little carbon monoxide CO is generally formed :



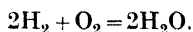
When the gas is shaken with water, a little carbon dioxide dissolves forming a solution of the very weak and unstable carbonic acid H_2CO_3 , which changes the blue colour of litmus to a port-wine red colour :



If another jar of carbon dioxide is prepared and the gas is shaken with lime water, this becomes milky from the formation of a precipitate of calcium carbonate CaCO_3 :



(4) A jet of hydrogen gas, prepared by the action of dilute sulphuric acid on zinc (see p. 162), burns in a jar of dry oxygen, producing water which condenses as a dew on the inside of the jar (Fig. 86) :



If a jet of oxygen is thrust into an inverted jar of hydrogen burning at the mouth, the oxygen takes fire and continues to burn in the atmos-

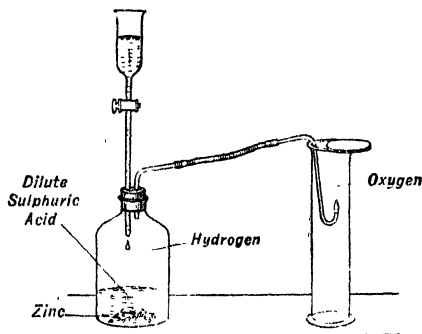


FIG. 86.—Hydrogen burning in oxygen.

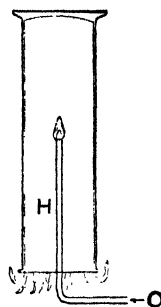


FIG. 87.—Oxygen burning in hydrogen.

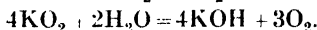
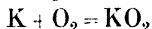
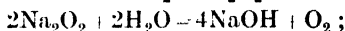
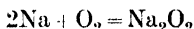
phere of hydrogen (Fig. 87). The terms *combustible* and *supporter of combustion* are therefore relative.

(5) Dry barium or strontium chlorate is heated in a vertical spoon until it evolves oxygen freely. A globe of coal gas is then lowered over the spoon (Fig. 88). The oxygen from the chlorate, if the latter is sufficiently heated, takes fire, and burns violently in the coal gas, the flame being coloured intensely green or crimson by the volatile barium or strontium compounds, respectively.

Combustion of metals in oxygen.—Some metals when strongly heated burn in oxygen to form oxides. These oxides are nearly always *basic oxides*, *i.e.* oxides which form salts with acids (p. 74). Other metals do not burn in oxygen, but combine with it on heating to form oxides.

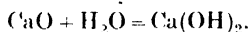
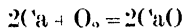
(1) Sodium and potassium, when heated in iron deflagrating spoons until they begin to burn and then lowered in *dry* jars of oxygen, burn with bright yellow and lilac flames, respectively, forming orange-yellow

solid higher oxides, sodium peroxide Na_2O_2 and potassium dioxide KO_2 . These *when cold* may be dissolved in water with evolution of oxygen and formation of alkaline solutions which turn red litmus blue and contain sodium and potassium hydroxides :

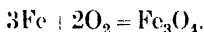


(2) Magnesium ribbon held in crucible tongs, ignited in air and inserted into a jar of oxygen, burns with a blinding white light, forming white solid magnesium oxide MgO , which is a sparingly soluble basic oxide and turns moist red litmus paper blue.

(3) A piece of calcium when strongly heated in an iron deflagrating spoon burns brightly in oxygen, forming calcium oxide CaO , which turns moist red litmus blue :



(4) A spiral of iron wire tipped with a bit of burning wood burns brilliantly, giving off bright sparks, when lowered into bottle of oxygen (Fig. 89). Ferrosoferric oxide Fe_3O_4 formed in fused globules, which fall on a layer of sand. It has no action on litmus :



Since ferrosoferric oxide may be regarded as a compound of ferrous oxide and ferric oxide, $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$, it is sometimes called *mixed oxide*.

Heat of combustion.—By the combustion of substances in oxygen large amounts of heat are given out. In everyday life we make use of the combustion of coal or gas in air (containing free oxygen) as a source of heat. Chemical reactions accompanied by an *evolution of heat* are called **exothermic reactions**.

In the decomposition of mercuric oxide heat must be supplied, and a reaction which is accompanied by an *absorption of heat* is called an **endothermic reaction**.

Tests for oxygen.—A test for pure oxygen (or a *large* proportion of oxygen mixed with an indifferent gas such as nitrogen) is the kindling

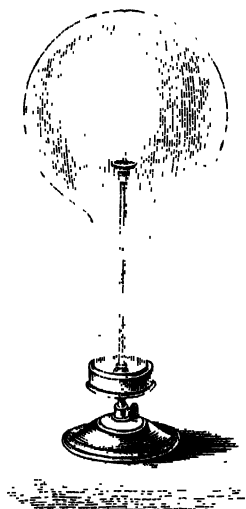


FIG. 88.—Apparatus for combustion

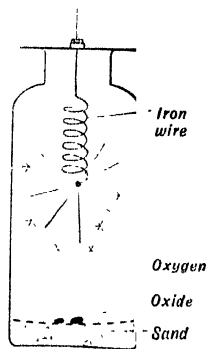
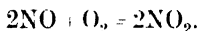


FIG. 89.—Iron wire burning in oxygen.

of a glowing chip of wood ; the only other gas which responds to this test and might be mistaken for oxygen is nitrous oxide N_2O . The two are distinguished by the fact that nitrous oxide is much more soluble than oxygen in water, and by the formation of red nitrogen dioxide NO_2 with free oxygen but not with nitrous oxide (unless it contains some free oxygen) :

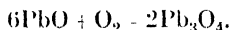


The nitric oxide test will detect free oxygen when present in a mixture which does not respond to the glowing chip test.

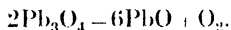
Determination of oxygen.—Oxygen is absorbed from gaseous mixtures in gas analysis by : (i) a solution of pyrogallol and caustic potash, which turns black ; (ii) phosphorus (this does not glow in pure oxygen) ; (iii) an acid solution of chromous chloride, which turns from blue to green owing to the formation of chromic chloride : $4CrCl_2 + O_2 + 4HCl = 4CrCl_3 + 2H_2O$; (iv) by mixing the gas with excess of hydrogen and sparking in a eudiometer, or adding enough hydrogen to form a non-explosive mixture and passing over platinised asbestos at a dull-red heat (or gently heated palladium), when water is formed ; one-third of the contraction of the gas then represents the oxygen contained in it : $2H_2 + O_2 = 2H_2O$ (liquid). The last method can be used only in the absence of other gases which react with either oxygen or hydrogen under the conditions of experiment (*e.g.* hydrocarbons or nitrous oxide).

Oxygen from air.—Oxygen may be obtained from the atmosphere, which is a mixture of oxygen and nitrogen (and a little argon), by heating mercury in a confined volume of air, when the oxygen forms mercuric oxide (Lavoisier's experiment, p. 33), and then heating the oxide strongly when pure oxygen is evolved (p. 14).

If yellow lead monoxide or massicot PbO is *carefully* heated in an iron dish and freely exposed to air, it takes up oxygen and forms red lead, the atmospheric nitrogen being unabsorbed :



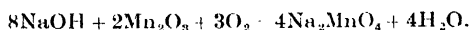
Red lead on heating more strongly decomposes into massicot and oxygen :



When steam is passed over sodium manganate heated to dull redness in a copper tube, oxygen is evolved :



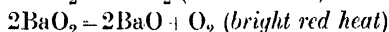
By passing air over the heated mixture oxygen is taken up and sodium manganate is formed, the nitrogen passing on :



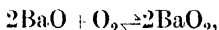
The manganate may now be decomposed by heating in a current of steam, when the oxygen taken up from the air is liberated by the first reaction, and the processes may be repeated.

Barium monoxide or baryta BaO takes up oxygen from air when heated to *dull redness*, forming barium peroxide BaO_2 . The nitrogen is

not absorbed. Barium peroxide on heating to *bright redness* evolves pure oxygen, leaving barium monoxide. The two reactions :



can both take place under suitable conditions, and each reaction may be said to be a reversible reaction. This is expressed by writing the equation in the form :



the arrows showing that it may take place in either direction.

These reactions were the basis of the now obsolete **Brin process**. In this two different *pressures* were used instead of two different *temperatures*.

Baryta was heated to dull redness in purified air in iron retorts under pressure, when it absorbed oxygen forming barium peroxide. The atmospheric nitrogen was removed by a pump and the pressure reduced, when the peroxide decomposed, evolving pure oxygen.

Barium peroxide heated in a closed vessel at a constant temperature decomposes into baryta and oxygen. The oxygen molecules by collision with the baryta form barium peroxide again. A state of equilibrium is set up at a definite pressure of oxygen. If the pressure of oxygen is raised the collisions become more frequent, combination takes place, and oxygen is absorbed by the baryta. If the pressure of the oxygen is decreased, more peroxide decomposes, since less oxygen returns to it by collisions, and if gas is *continuously* pumped off all the peroxide is decomposed (see p. 290).

Technical preparation of oxygen.—Various methods have been used for the large-scale production of oxygen, but at present the two mostly used are the electrolysis of water (with simultaneous production of hydrogen), and the fractional distillation of liquid air.

One type of electrolytic apparatus consists of an iron tank containing a solution of caustic soda, in which are immersed a number of iron bell-jars, each provided with an insulated iron electrode dipping below the mouth of the bell. The electrodes are connected to the positive and negative poles of a dynamo, and the oxygen and hydrogen gases liberated pass inside the bell-jars and are led off through pipes.

Most of the oxygen made is obtained from liquid air. This is obtained, as described on p. 131, in an apparatus using the Joule-Thomson effect of free expansion.

In the **Claude process** the compressed air is used to work an expansion engine, when the heat equivalent of the work done is extracted from the air ; in this way it can be cooled through 75°.

The liquid air is a mixture of liquid nitrogen (boiling point -196°) and liquid oxygen (boiling point -183°). The nitrogen is more volatile and tends to boil off first in evaporation, although some oxygen evaporates with it. The separation of the two gases is brought about by letting the evolved gas bubble through liquid air rich in oxygen in a tall

rectifying column. The oxygen in the gas condenses and nearly pure nitrogen gas passes off, leaving nearly pure liquid oxygen which is then evaporated. At first sight it might seem possible to obtain oxygen from liquid air by allowing the more volatile nitrogen to boil off, leaving the liquid oxygen. The boiling points are too close to allow of this and the figures in the table below (from Linde's experiments) show that such a process would be attended by great loss and could never give oxygen pure enough for industrial use. (Weight percentages are shown.)

% liquid not evaporated	% O ₂ in liquid	% O ₂ in gas evaporating	% original O ₂ left in liquid
100	23	7.5	100
50	37.5	15	80
30	50	23	65
20	60	34	52
10	77	52	33
5	88	70	19

The process introduced by Linde in 1902 uses *fractional distillation* in a rectifying column in which the escaping gas is scrubbed by liquid passing in the other direction. Claude in 1906 introduced the principle of liquefying the air in stages, obtaining two liquids, one rich in oxygen and the other in nitrogen, which are poured into the rectifying column at the appropriate places. The column shown in Fig. 90 is used in the Claude processes.

Compressed air which has been cooled by expansion in an engine enters at *A*, when it partly liquifies and enters a vessel containing two sets of vertical tubes *B*. Liquid richer in oxygen drains into *A* while gas richer in nitrogen rises and passes through the outer ring of tubes. Both sets of tubes are cooled in liquid oxygen in *S*. The part liquefied in the outer ring is richer in nitrogen (since the gas is under increased pressure it liquifies at the temperature of the liquid oxygen) and the liquid rich in nitrogen collects in the annulus *C*. This nitrogen-rich liquid is sent to the top of the upper rectifying column, where the nitrogen tends to boil off. Into this column the oxygen-rich liquid from *A* is discharged at *L*. The liquid running down the column *D* meets gas rising from *S*. The liquid loses its more volatile constituent nitrogen as gas, whilst the rising gas is robbed of its

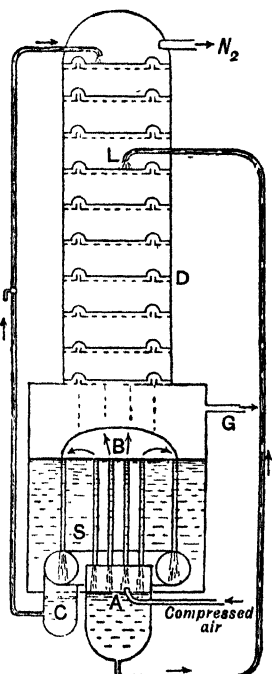


FIG. 90.—Liquid air fractionating column.

less volatile constituent oxygen by the liquid, the heat of condensation of the oxygen serving to evaporate the nitrogen. Finally, nitrogen gas escapes at the top of the column and liquid oxygen drops into *S* where it evaporates, the gas passing through heat interchangers to compressors, which pump it into steel cylinders for sale. In practice it is not economical to make both pure oxygen and pure nitrogen with the same apparatus; when oxygen is made a nitrogen-rich gas is waste and when nitrogen is made an oxygen-rich gas is waste. Sometimes another fractionating column below the apparatus is used.

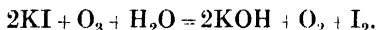
Oxygen gas is used in blowpipes with hydrogen, coal gas and acetylene for welding and cutting metals (p. 169). It is used in some industrial processes and medicinally in cases of pneumonia and gas poisoning, and mixed with nitrous oxide, ether vapour or other anaesthetic. Some carbon dioxide is often mixed with the oxygen, as this stimulates breathing, and carbon dioxide is also used in cases of poisoning and collapse for restoring respiration. Liquid oxygen mixed with powdered charcoal has been used as an explosive.

OZONE

History.—Van Marum in 1785 found that oxygen gas through which an electrical discharge had passed had a peculiar smell and tarnished mercury. This smell is easily noticed in a physics laboratory when experiments on electrostatics are in progress. Cruickshank in 1801 observed the same smell in electrolytic oxygen, but the fact that it is due to a particular gas was first recognised in 1840 by Schönbein, who gave the substance the name **ozone** (Greek, *ozō*, I smell). He found that it is also produced by the slow oxidation of phosphorus in moist air, is decomposed by heat, and is a powerful oxidising agent, liberating iodine from potassium iodide solution.

Occurrence.—The invigorating properties of sea air are popularly attributed to "ozone" and this is produced by electric discharges in the atmosphere and especially by the action of ultra-violet light from the sun on the oxygen in the upper layers of the atmosphere. According to Paneth (1938) ordinary air contains one millionth of a per cent by volume of ozone. If present in air in larger amounts than 1 in 20,000 ozone has an irritating action on the mucous membranes and is poisonous.

Preparation of ozone.—A few sticks of phosphorus freshly scraped under water are placed in a stoppered bottle with a little water. When the fumes have subsided a piece of paper dipped into a solution of potassium iodide and starch ("starch-iodide paper") introduced into the bottle is turned blue from liberation of iodine by the ozone formed:



It is difficult to obtain pure ozone (which is explosive), but a mixture of ozone with oxygen or with air is easily made by the action of a "silent electric discharge" on these gases. The best apparatus for the experiment is Brodie's ozoniser (Fig. 91). The oxygen or air is passed slowly

through the annular space between two glass tubes, the inner filled with dilute sulphuric acid or copper sulphate solution, and the whole apparatus placed in a jar of the liquid. The wires from a coil dip into the two liquids, which form electrodes and at the same time serve to cool the apparatus. The gas is conducted away through glass tubes with ground-glass joints, or joints of ordinary corks. Rubber is quickly destroyed by ozone.

Siemens' ozoniser (Fig. 92) consists of two concentric glass tubes, the outer covered and the inner lined with tinfoil to form the electrodes.

The formation of ozone is shown by the smell of the issuing gas, which may contain about 5 per cent of it by volume. By cooling the whole apparatus at 0°, using a powerful coil, and avoiding sparks, as much as 25 per cent by weight of the oxygen may be converted into ozone.

Ozone is formed by the action of ultra-violet light from a quartz mercury lamp on oxygen, and is produced in some chemical reactions, e.g. by the action of concentrated sulphuric acid on barium peroxide and by heating periodic acid; ozone is also present in the air round hydrogen and hydrocarbon flames.

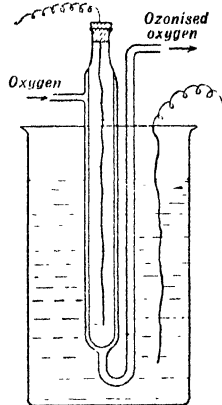


FIG. 91 - Brodie's ozoniser.

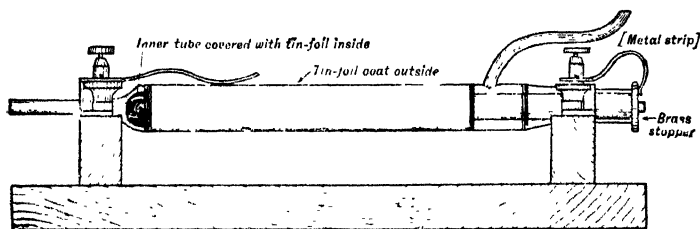
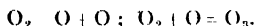


FIG. 92. - Siemens' ozoniser.

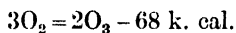
Warburg found that ultra-violet light of wave-length 209m μ produces ozone, and since the line 185 m μ is the only one from the mercury lamp strongly absorbed by oxygen it is probably the chemically active one, corresponding (p. 216) with the energy 165 k.cal. This could dissociate the O₂ molecule into normal atoms (118 k.cal.). Warburg found that two molecules of ozone are formed per absorbed energy quantum. It may be assumed that the formation of ozone, both by the action of the electric discharge and of ultra-violet light on oxygen, involves the dissociation of the oxygen molecules into atoms, which then react with oxygen molecules to form ozone :



This agrees with the quantum yield found by Warburg if one molecule is dissociated per quantum (p. 216) : $\text{O}_2 + h\nu \rightarrow 2\text{O}$.

Ozonised oxygen is formed by the electrolysis of sulphuric acid (sp. gr. 1.1). A good yield is obtained with a heavy current and an anode (positive electrode) composed of a narrow platinum tube coated with glass, having a narrow line of metal exposed, and cooled by a stream of calcium chloride solution at -14° .

When ozonised oxygen is passed through a tube cooled in liquid air a cornflower-blue liquid separates, which is a solution of ozone in liquid oxygen. By strong cooling and evaporating under low pressure, violet-black crystals of pure solid ozone are formed, which on raising the temperature melt at -249.7° , and the liquid boils at -112.4° forming a dark-blue gas which is pure ozone. The density, as determined by Dumas' method, corresponds with the formula O_3 . Pure ozone is very explosive, since it is strongly endothermic with respect to oxygen (O_2):



Properties of ozone.—The properties of ozone to be described refer mostly to a mixture of ozone with oxygen or air.

Ozone is more soluble than oxygen in water: 1 vol. of water at 0° dissolves 0.49 vols. of ozone. It is more soluble in glacial acetic acid and in carbon tetrachloride than in water. Ozone is decomposed by heat and when the gas from an ozoniser is passed through a glass tube heated at about 300° all the ozone is converted into oxygen:



Ozone is a powerful oxidising agent and liberates iodine from a solution of potassium iodide:



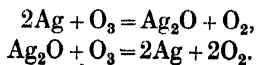
In this reaction the volume of the gas remains unchanged, since one atom of oxygen in the ozone molecule oxidises the iodide and the other two atoms form a molecule of ordinary oxygen.

Chlorine, bromine, hydrogen peroxide and nitrogen dioxide also liberate iodine from potassium iodide; they are distinguished from ozone by the tests described on p. 157.

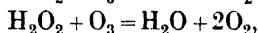
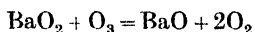
Ozone has a remarkable action on mercury; when ozonised oxygen is passed into a clean dry flask containing a little mercury, the meniscus is destroyed and the metal adheres to the glass. On shaking with water, the mercury recovers its original form. According to Hodgson (1924) this action is due to oxidation to Hg_2O which dissolves in mercury.

Ozone is decomposed when shaken with powdered glass, and catalytically in contact with metallic silver and platinum, and with manganese dioxide, lead dioxide, and silver, cobalt and iron oxides.

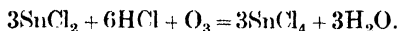
Warm silver is blackened by ozone, and silver oxide is probably alternately formed and reduced:



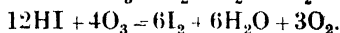
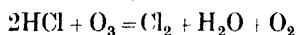
Barium and hydrogen peroxides react with ozone :



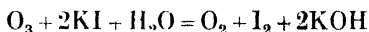
but the gas has no action on chromic acid or potassium permanganate. Sulphur dioxide is oxidised to the trioxide : $3\text{SO}_2 + \text{O}_3 = 3\text{SO}_3$. This is one of the few reactions in which the ozone molecule oxidises as a whole ; another is with stannous chloride solution :



Ozone bleaches indigo solution and vegetable colours, and converts moist sulphur, phosphorus, and arsenic into their highest oxy-acids. It liberates halogens from their hydrides :

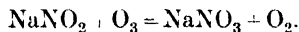


The liberation of iodine from potassium iodide :

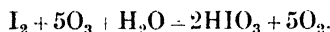


occurs in a neutral solution, which then becomes alkaline. If a piece of neutral litmus paper is moistened with potassium iodide solution and exposed to a gas containing ozone, the wetted portion is turned blue owing to liberation of alkali.

In the determination of ozone, the iodine liberated from a *neutral* solution of potassium iodide may be titrated with sodium thiosulphate after slight acidification. Another method depends on the oxidation of sodium nitrite solution :

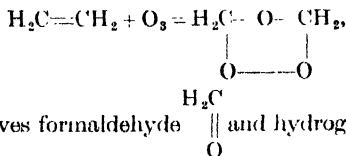


Moist iodine is oxidised by ozone to iodic acid :



Dry iodine is converted into a yellow powder I_4O_9 without change of volume of the gas : $2\text{I}_2 + 9\text{O}_3 = \text{I}_4\text{O}_9 + 9\text{O}_2$. An alkaline solution of potassium iodide is oxidised to iodate (KIO_3) and periodate (KIO_4).

Ozone is used in oxidising some organic compounds : it combines with double linkages to form ozonides, which are decomposed by water, *e.g.* with ethylene :



which with water gives formaldehyde and hydrogen peroxide H_2O_2 .

The formula of ozone.—Schönbein found that ozonised oxygen passed through a glass tube heated to 400° loses its smell and action on potassium iodide, and the gas then appears to be ordinary oxygen.

Marignac and de la Rive (1845) and Shenstone and Cundall (1887), found that pure dry oxygen can be ozonised by an electric discharge. Briner and Durand (1907) converted a confined volume of oxygen completely into a blue liquid mixture of ozone and oxygen by the silent discharge in a tube of dry oxygen, cooled in liquid air. These experiments show that ozone is merely a modification of oxygen.

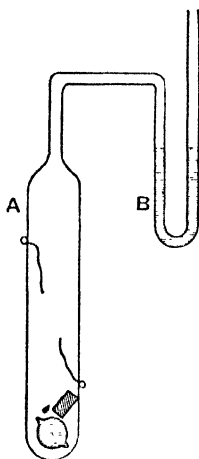
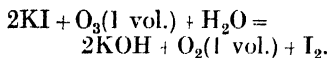


FIG. 93.—Andrews and Tait's experiments on ozone

This conclusion was also reached by Andrews (1856), who dried electrolytic oxygen by means of sulphuric acid and then passed it through two bulb-tubes, *A* containing potassium iodide solution, and *B* concentrated sulphuric acid. The increase in weight of the two bulbs was exactly equal to the oxygen equivalent ($O = I_2$) of the iodine liberated. The bulb *A* was then replaced by a glass tube heated to 400° . The weight of the bulb *B* remained constant, showing that the gas contained no hydrogen. Andrews also found that ozone prepared in different ways (electric discharge, electrolysis, oxidation of phosphorus) has the same properties.

Andrews and Tait (1860) filled a tube *A* (Fig. 93) with dry oxygen, which communicated with a sulphuric acid manometer *B*. Sulphuric acid is without action on ozone. After the silent discharge, a maximum contraction of one-twelfth was observed, hence ozone is denser than oxygen. When the tube was heated to 300° , the original volume was restored. A glass bulb of mercury broken inside the tube by means of a short length of glass rod which could be shaken on it, was converted into a black powder, and a variable volume of gas remained. A bulb of potassium iodide solution broken in the gas produced iodine, and the volume of gas remained unchanged, although it no longer expanded after heating to 300° and was therefore completely converted into oxygen.

Odling in 1861 pointed out that the reactions could be explained on the assumption that the formula of ozone is O_3 :



The formula $O_{2.5}$ will obviously give the same result, but O_3 is the simplest, and there were no experiments pointing to a more complicated formula.

Odling's formula was confirmed by Soret in 1866-68 by two sets of experiments. Soret pointed out that oxidisable bodies which destroy

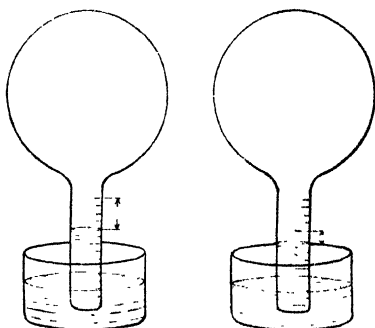


FIG. 94.—Soret's first experiments on ozone.

ozone without change of volume, such as those used by Andrews and Tait, give no indication of the density of ozone.

In order to find the volume of ozone in the mixture, some solvent or absorbent is necessary which takes up the whole of the ozone without liberating oxygen (as is the case with potassium iodide). By comparing the contraction on absorption with the expansion on heating (or contraction on ozonisation) it would be possible to determine the formula.

Suppose that 100 vols. of oxygen on ozonisation contract to 90 vols. If ozone is O_3 , the equation $3O_2 = 2O_3$ shows that 30 vols. of oxygen form 20 vols. of ozone, giving $70 + 20 = 90$ vols. of gas in all. On heating, the 20 vols. of ozone give 30 vols. of oxygen, an expansion of 10 vols. If the ozone were absorbed, there would be a contraction of 20 vols. If the formula of ozone is O_4 , 20 vols. of oxygen give 10 vols. of ozone : $2O_2 = O_4$, giving $80 + 10 = 90$ vols. of gas ; the contraction on absorption would be 10 vols. and the expansion after heating 10 vols.

The formula O_3 requires that the contraction on absorption shall be double the expansion after heating.

Soret found that suitable absorbents for ozone were certain essential oils, such as oil of cinnamon and oil of turpentine. He took two flasks, of 250 ml. capacity filled with ozonised oxygen over water (Fig. 94). In one flask the ozone was absorbed by turpentine, when dense white fumes were produced; in the other it was decomposed by heating the flask by a flame. The contraction in the first flask was found to be almost exactly double the expansion (after the gas had cooled) in the second. Thus, Odling's formula O_3 confirmed.

The apparatus shown in Fig. 95, devised by Newth (1896), consists of two concentric glass tubes, the inner fitted into the outer by a ground-glass joint. The inner tube contains dilute sulphuric acid and the apparatus, previously filled with dry oxygen, is supported in a jar of water and crushed ice. Two wires from a coil dip into the liquids. By means of projections from the inner and outer tubes a thin glass tube *a* containing oil of turpentine or oil of cinnamon is held in position in the annular space. The manometer containing concentrated sulphuric acid* coloured with indigo communicates with the apparatus, and the oxygen is ozonised. The contraction is read off on the gauge. The inner tube is then twisted so as to break the tube of oil of turpentine, and after absorption the further contraction is read off. It will be found that the contraction on absorption is twice the contraction on ozonisation, *i.e.*

* The acid does not act on ozone; mercury cannot be used (p. 152), and ozone is rather too soluble in water.

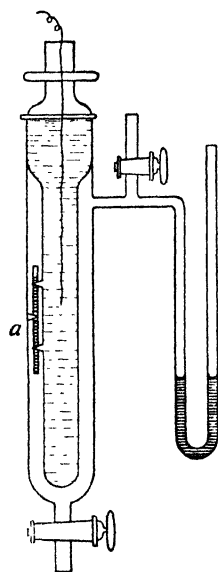


FIG. 95.- Newth's apparatus

double the expansion which would have occurred on decomposing the ozone by heat. In each case, before reading the volume, adequate time must be allowed for the gas to assume a constant temperature.

Soret in his second research (1868) used Graham's law of diffusion. If ozone has the formula O_3 (density 24, $H = 1$) it should diffuse rather more slowly than carbon dioxide (density 22) but more rapidly than chlorine (density 35.5). The diffusion rates are inversely proportional to the square roots of the densities :

$$\frac{\text{Rate of diffusion of } CO_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{22}}; \quad \frac{\text{Rate of diffusion of } Cl_2}{\text{Rate of diffusion of } O_3} = \frac{\sqrt{24}}{\sqrt{35.5}}$$

Soret allowed the gases to diffuse into pure oxygen and measured the *relative diffusion* v/V of each gas mixed with oxygen, where v is the volume of gas diffusing and V the total volume present in the original mixture. The rate of diffusion of oxygen in both directions was the same : the rates of diffusion of the other gases were (i) proportional to the numbers of molecules present in a given volume (measured by V) and (ii) inversely proportional to the square roots of the densities. The ratios v/V were therefore inversely proportional to the square roots of the densities of the diffusing gases.

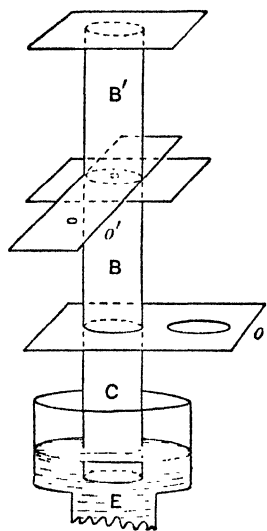


FIG. 96.—Soret's diffusion apparatus.

The apparatus (Fig. 96) consisted of three glass tubes B' , B and C , placed over sulphuric acid in E and separated by sliding glass plates with holes, so that the tubes could be put in communication or separated. B' was filled with pure oxygen. B was first full of acid and the mixture of one of the gases with oxygen, prepared in C , was transferred to B by sliding the glass partition o . The glass plates between B and B' had perforations which could be brought between the two cylinders by sliding the plate o' . Diffusion from B

to B' was allowed to go on for forty-five minutes, when the plate o' was slid back and the cylinders again isolated. The gas in B' could be driven out into a solution of baryta when carbon dioxide was diffused, or potassium iodide for chlorine or ozone. The ratio of the ozone in the original gas and in the gas in B' was determined from the ratio of the amounts of iodine liberated by the gases. If u, u' are the amounts of iodine liberated by the gas in B' and that remaining in B , respectively, then $v/V = u/(u + u')$. The relative rates of diffusion were found to be : chlorine, 0.227 ; ozone, 0.271 ; carbon dioxide, 0.290.

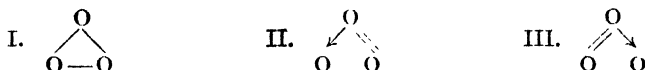
The ratio of these values for ozone and chlorine is $227/271 = 0.838$. The inverse ratio of the square roots of the densities, assuming that ozone is O_3 , is $\sqrt{24/35.5} = 0.822$. The diffusion ratio for carbon dioxide and ozone is

271/290 = 0.93, whilst the inverse ratio of the square roots of the densities, again assuming O_3 , is $\sqrt{22/24} = 0.95$. The agreement is to 3 per cent, which is satisfactory as the ozonised oxygen contained only 5 per cent of ozone by volume.

Brodie (1872) in a very careful research showed that the only formula of ozone which agrees with all its reactions is O_3 .

Ladenburg in 1898 obtained nearly pure ozone by the evaporation of the liquid and compared the times of effusion of equal volumes of this gas and of oxygen in a Bunsen's effusion apparatus; he found a density of 22, in satisfactory agreement with the formula O_3 , and the density 24 was found in 1922 with pure ozone in a Dumas' apparatus by Riesenfeld and Schwab.

The shape of the ozone O_3 molecule is definitely known to be triangular from electron-diffraction experiments (p. 439). The ring formula with single bonds I is not in agreement with the absorption spectra and the bond lengths (1.26 Å., much shorter than 1.46 Å. for O—O). It is supposed that the molecule has one double bond and one coordinate link (p. 413) and the actual state is a resonance hybrid (p. 437) between such forms as II. and III. The bond angle is doubtful, values of 127° and $51\frac{1}{2}^\circ$ being given by different interpretations of electron diffraction results.



Tests for ozone.—The difficulty of detecting ozone when there is not enough to show its characteristic smell (1 volume in 500,000) is that chlorine, bromine, hydrogen peroxide vapour, and some oxides of nitrogen (N_2O_3, NO_2, N_2O_4) also liberate iodine from potassium iodide.

Test papers prepared by soaking filter paper with alcoholic solutions of the reagents below react as stated; they are unaffected by hydrogen peroxide :

	<i>Ozone</i>	<i>Halogens</i>	<i>Oxides of nitrogen</i>
Tetramethyl-base -	violet	blue	straw-yellow
Benzidine - -	brown	blue, then red	blue

Hydrogen peroxide vapour and oxides of nitrogen may be removed by passing the gas through a solution of chromic acid.

Hydrogen peroxide and ozone are decomposed by passing the gas over manganese dioxide, whilst oxides of nitrogen pass on and will decolorise dilute permanganate solution. The latter will absorb oxides of nitrogen and hydrogen peroxide and allow ozone to pass. Hydrogen peroxide is then detected by bubbling the gas through a solution of potassium ferri-cyanide and ferric chloride, which is turned blue.

Technical utilisation of ozone.—Air or oxygen is ozonised on the technical scale by the silent electric discharge. The Siemens and Halske

ozoniser (Fig. 97) consists of a battery of glass or porcelain tubes with internal tubes of aluminium, enclosed in an earthed iron tank of water to cool the apparatus.

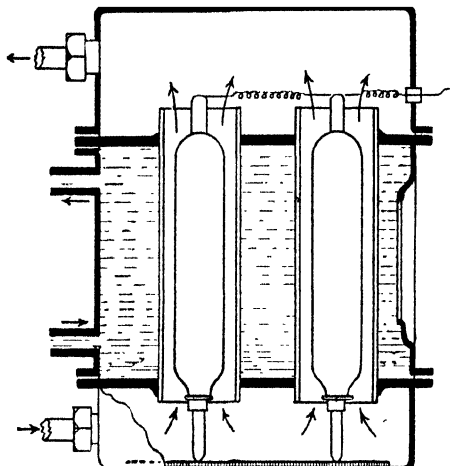


FIG. 97.—Siemens and Halske ozoniser.

The aluminium tubes are charged to a potential of 8000–10,000 volts, each battery of 6–8 tubes requiring half a kilowatt of power. The Ozonair apparatus consists of two sheets of aluminium gauze separated by a plate of insulator, several units being enclosed in a case and alternate plates charged and earthed. The best production amounts to about 40–60 gm. of ozone per kilowatt-hour, at a concentration of 2 gm. of ozone per cu. m. of air. With pure oxygen, 120–180 gm. are obtained. The yields are about 5 and 15 per cent of the theoretical with air and oxygen, respectively.

Ozonised air is used in the sterilisation of water, when it is bubbled through the filtered water in a tall column (2 gm. of ozone per cu. m. of water): also for purifying air (*e.g.* in underground railways) and for oxidation processes (*e.g.* *iso*-eugenol to vanillin). The purification of water is its most important use: the plant supplying Paris deals with 24,000,000 gallons daily.

CHAPTER XII

HYDROGEN

History.—Hydrogen gas was prepared by Boyle from steel filings and hydrochloric acid, and from iron nails and dilute sulphuric acid (p. 36), although Van Helmont (d. 1644) had described an inflammable gas (*gas pingue*). It was carefully investigated by Cavendish in 1766 and called by him *inflammable air*.

Occurrence.—Free hydrogen is said to occur in small quantities in some volcanic gases : those evolved in the eruption of Mt. Pelée in 1902 contained 22·3 per cent hydrogen. It also occurs in small cavities in rock-salt, and various minerals and rocks, such as apatite, serpentine, gneiss, blue-clay, Peterhead granite, basalt, and beryl, evolve hydrogen on heating. Meteorites composed chiefly of iron with nickel and cobalt contain hydrogen. The spectroscope shows that the outer atmosphere of the sun consists largely of hydrogen ; this gas is the chief constituent of the solar prominences, which may reach out from the sun's disc sometimes as far as 500,000 miles into space. Hydrogen is produced in certain types of fermentation of carbohydrates brought about by specific bacteria.

Hydrogen in combination is more common. With oxygen it forms water H_2O , and with carbon a large number of compounds called hydrocarbons ; the gas issuing from fissures in coal often consists of nearly pure methane (CH_4) and more complicated hydrocarbons make up petroleum. All animal and vegetable matter, and coal, contain hydrogen, and gaseous hydrogen compounds found in nature are hydrogen sulphide (H_2S) and phosphide (PH_3), ammonia (NH_3), and in volcanic gases hydrogen chloride (HCl), bromide (HBr), and iodide (HI).

Preparation.—Hydrogen may be obtained in a large number of different ways *only a few of which are convenient for the laboratory preparation* ; some are used in industry and not in the laboratory. These methods may be classified as follows :

1. From *water* :
 - (a) by *electrolysis* ;
 - (b) by the action of *metals* ;
 - (c) by the action of *carbon*.
2. From *acids* by the actions of *metals*.
3. From *alkalis* by the action of *metals*.
4. Miscellaneous industrial processes.

Hydrogen from water. The different methods are :

(1) *By electrolysis.* The water voltameter is explained in Chapter IV. Water acidulated with dilute sulphuric acid is commonly used, but a dilute solution of sodium or barium hydroxide may be used.

Rather less than 1 vol. of oxygen to 2 vols. of hydrogen is evolved, partly on account of the greater solubility of oxygen in water compared with hydrogen (1.8 to 1), and partly owing to oxidation of the sulphuric acid to persulphuric acid $H_2S_2O_8$ at the anode. Some hydrogen peroxide H_2O_2 is formed at the cathode. The presence of these oxidising agents may be shown by adding a solution of potassium iodide and starch, when a blue colour, due to liberation of iodine, appears. The oxygen may also contain a little ozone. If the liquid is electrolysed hot or phosphoric acid is used instead of sulphuric acid, no ozone is formed and the volumes are nearly in the ratio 2 : 1.

If the anode consists of a pool of zinc amalgam in acidulated water, the oxygen liberated combines with the zinc and only hydrogen is evolved from the platinum cathode (Bunsen's voltameter).

Pure hydrogen is best prepared by the electrolysis with nickel electrodes of warm saturated barium hydroxide solution. The gas is passed over hot platinum gauze (not platinised asbestos, which forms a trace of silicon

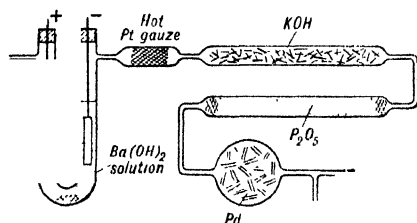


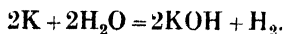
FIG. 98.—Preparation of pure hydrogen.

hydride) to burn any oxygen in it, then dried by potassium hydroxide (*not* concentrated sulphuric acid, which forms a little sulphur dioxide by reduction) and pure redistilled phosphorus pentoxide. The gas may then contain a little nitrogen (from air leaks). It is passed into an exhausted hard-glass bulb containing metallic palladium, which

is gently heated. Only the hydrogen is absorbed by the palladium. The nitrogen is pumped out and on strongly heating the palladium, pure hydrogen is evolved (Fig. 98)

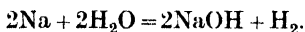
(2) *By the action of metals.* The metals lithium, sodium, potassium and calcium act on water at the ordinary temperature, the first three violently but calcium only slowly unless the water is hot, when the action is more vigorous.

The heat evolved sets fire to the hydrogen given off from a *small* piece of potassium floating on water, the gas burning with a flame coloured lilac by potassium vapour : *



* The fused globule of caustic alkali left on the water after the action of sodium or potassium is usually thrown out of the liquid with a sharp crack on cooling, so that it is safer to place a bell-jar (open at the top) over the dish. Serious results

The reaction with sodium is less violent and the hydrogen does not ignite and burn unless the metal is kept in one place on the surface of starch-jelly, when the hydrogen burns with a flame coloured yellow by sodium vapour :

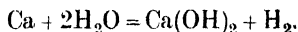


Sodium amalgam acts slowly on water. The amalgam containing more than 1 per cent of sodium is solid at the ordinary temperature.

Small pieces of clean sodium are pressed one by one under the surface of dry mercury in an iron mortar. Each piece dissolves with a flash of light, poisonous fumes of mercury vapour being evolved. The amalgam is placed in a porcelain crucible in a basin of water, under an inverted jar of water. Gradual evolution of hydrogen occurs, metallic mercury being left.

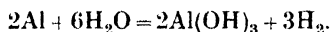
H. B. Baker and L. H. Parker (1913) found that if the amalgam and water are very pure, the action is slow, bubbles of gas appearing only at isolated points on the surface of the amalgam. If ordinary distilled water is added, the evolution of gas is accelerated, apparently owing to the presence of hydrogen peroxide in the water.

A piece of calcium may be used in the experiment :

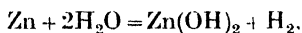


The gas obtained from calcium may contain a little acetylene, from some calcium carbide in the metal.

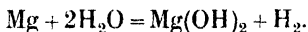
Cold water is decomposed by amalgamated aluminium (made by rubbing aluminium foil with damp mercuric chloride) :



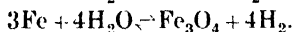
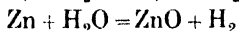
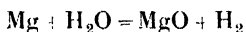
Hot water is decomposed by zinc-copper couple (made by pouring a solution of copper sulphate over granulated zinc) :



and boiling water is slowly decomposed by magnesium powder :



Steam is decomposed by heated magnesium, zinc and iron :



The action with magnesium has been described on p. 39 ; the hydrogen may be collected with a suitable apparatus (see Partington, *School Course of Chemistry*, Chap. XIII).

The action of iron on steam is described on p. 39. It is reversible ; when steam is passed over heated iron the hydrogen formed tends to reduce the iron oxide again, and when hydrogen is passed over heated iron oxide the steam formed tends to oxidise the iron again.

follow the projection of the alkali into the eye or on the skin. All experiments with sodium and potassium, like those with phosphorus, require great care. Attempts to collect the hydrogen evolved with sodium usually result in explosions.

When a mixture of hydrogen and steam in the correct ratio is passed over a heated mixture of iron and oxide of iron, no change occurs either in the gas or in the solid mixture, and the one mixture is therefore in chemical equilibrium with the other. The fact that such a state is possible depends on the reversibility of the reaction. *Equilibrium is attained when two opposing reactions proceed with equal velocities.* The same equilibrium state is reached by starting either with iron and steam or with iron oxide and hydrogen.

If a given weight of iron is taken and a *large excess* of steam passed over it, the red-hot iron will in the end be completely oxidised : a given weight of red-hot iron oxide when exposed to a current of hydrogen in excess of amount required by the chemical equation will in the end be completely reduced. This effect is sometimes called the *action of mass*.

Hydrogen from acids.—The usual *laboratory* method of preparation of hydrogen is to act upon granulated zinc in a flask or Woulfe's bottle

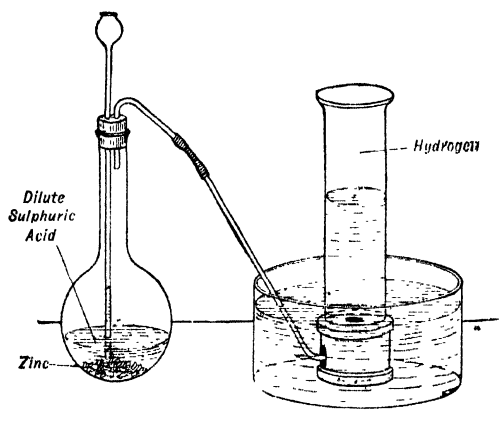
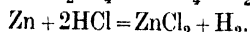
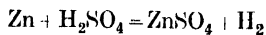


FIG. 99. —Preparation of hydrogen.

with dilute sulphuric acid (1 vol. conc. acid to 5 vols. of water) or dilute hydrochloric acid (1 vol. conc. acid to 4 vols. water), poured in through a thistle funnel (Fig. 99). Zinc sulphate or chloride is formed in solution and the hydrogen evolved is collected over water :



Instead of a flask a Kipp's apparatus (Fig. 23) may be used, the metal being in the central globe and acid poured in until the lower bulb is full and the metal covered. When the tap is closed evolution of gas continues until the liquid is forced by pressure partly into the upper globe and the metal is brought out of contact with the liquid, when the action ceases.

The Kipp's apparatus may be used for the generation of gas from any liquid reagent and a solid which can be obtained in the form of lumps which do not disintegrate in contact with the liquid, *e.g.* carbon dioxide

from marble and hydrochloric acid, and hydrogen sulphide from ferrous sulphide and hydrochloric acid.

The gas from commercial zinc and acid may be *purified* by passing over red-hot copper turnings, or through wash-bottles containing a saturated solution of potassium permanganate, followed by bottles containing a 5-10 per cent solution of silver nitrate. Impurities such as hydrogen sulphide, phosphide and arsenide, and oxides of nitrogen, sulphur dioxide, and volatile hydrocarbons, are removed. Unless hot copper is used, a little oxygen remains, but this may be removed by a solution of chromous chloride or by passing over red-hot copper. On a large scale, bleaching powder or a solution of bromine is used to remove arsenic compounds.

Hydrogen is *dried* by passing over granular calcium chloride, or broken sticks of potassium hydroxide, in a tower (Fig. 100): final drying may be effected by phosphorus pentoxide dusted over plugs of glass-wool in a tube. Sulphuric acid should *not* be used, as a little sulphur dioxide is formed: $\text{H}_2\text{SO}_4 + \text{H}_2 = \text{SO}_2 + 2\text{H}_2\text{O}$, unless the acid is cooled in a freezing mixture.

Since hydrogen is very much lighter than air it may also be collected by upward displacement (Fig. 101).*

Hydrogen is also evolved by the action of dilute hydrochloric or sulphuric acid on iron (which gives a rather impure gas with an unpleasant odour due to the presence of hydrocarbons, hydrogen sulphide, hydrogen phosphide and silicon hydride, from impurities in the metal) or magnesium (which is expensive but gives a pure gas), or by the action of hot concentrated hydrochloric acid on tin:

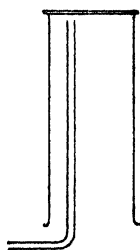
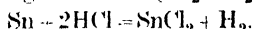
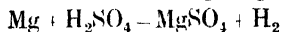
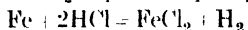
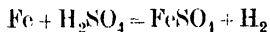


FIG. 101.—Collecting a gas by upward displacement

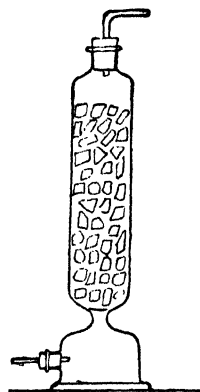


FIG. 100.—Drying tower.

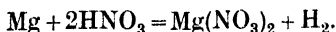
Before collecting hydrogen great care must be taken to ensure that all the air has been displaced from the apparatus since a mixture of hydrogen with air is explosive.

A little of the gas is first collected in a test-tube and a flame applied; the gas in the tube should burn slowly and quietly and not explode. (The mere

* The student may note that "upward displacement" is sometimes called "downward displacement of air", and "downward displacement" is sometimes called "upward displacement of air"! A diagram is usually advisable.

absence of explosion is misleading, since the first portion of gas collected may be air and the gas following this is highly explosive.)

Copper and lead are not dissolved by dilute acids with evolution of hydrogen, and the action of nitric acid on metals nearly always gives oxides of nitrogen, not hydrogen (p. 537). With magnesium and cold *very dilute* (1 per cent) nitric acid, hydrogen is evolved :



The rate of liberation of hydrogen with a particular metal depends on the *strength* of the acid (which must not be confused with the concentration).

Arrange three flasks with delivery tubes under burettes in a pneumatic trough (Fig. 102). In each place 5 gm. of zinc, and pour in 50 ml. of solu-

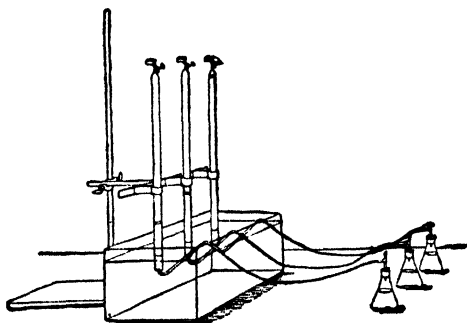
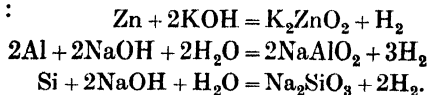


FIG. 102.—Experiment to compare rates of evolution of hydrogen by zinc from different acids.

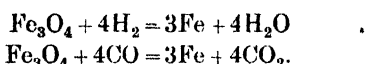
tions of hydrochloric (36.5 gm. per litre), sulphuric (49 gm. per litre), and acetic (60 gm. per litre) acids. All these contain 1 gm. of acidic hydrogen per litre. Add 1 ml. of dilute copper sulphate solution to each, and after a minute fit on the corks and observe the rates of collection of gas. The "strong" acids (hydrochloric and sulphuric) react much more rapidly than the "weak" (acetic), and hydrochloric acid more rapidly than sulphuric.

Hydrogen from alkalis.—Zinc, aluminium and silicon decompose potassium or sodium hydroxide solution, evolving hydrogen and forming solutions of potassium or sodium zincate, aluminate and silicate, respectively :

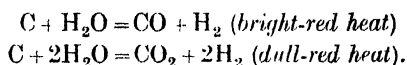


Industrial preparation of hydrogen.—The reaction between steam and iron is used for the technical preparation of hydrogen. Spongy iron from the reduction of spathic iron ore (ferrous carbonate) is heated to redness and steam passed over : $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2.$

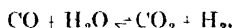
The hot ferrosiferrous oxide is then reduced with water gas :



Water gas is made by passing steam over red-hot carbon and is a mixture of carbon monoxide and hydrogen with a smaller amount of carbon dioxide :

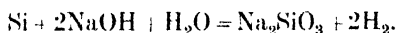


Hydrogen is also made from water gas. In one process the carbon monoxide is removed by strong cooling, when it liquefies (b.p. -191.5°) leaving the hydrogen gaseous (b.p. -253°). In another process, water gas is mixed with excess of steam and passed at 450° over a heated catalyst consisting mainly of oxide of iron (Fe_2O_3) with some oxides of nickel and chromium which act as "promoters", i.e. increase the activity of the catalyst. The carbon monoxide is mostly oxidised to carbon dioxide and more hydrogen is set free from the steam :

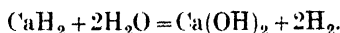


Since this reaction is reversible, excess of steam is used and a little carbon monoxide remains in the gas. The carbon dioxide is removed by absorption in water under 25 atm. pressure, and the carbon monoxide by absorption in ammoniacal cuprous formate solution under 200 atm. pressure. Large quantities of pure hydrogen are made in this way for the manufacture of synthetic ammonia (p. 522).

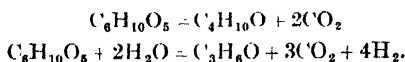
Hydrogen can be made on a semi-technical scale for filling military balloons (when cylinders of compressed gas are not available) by the action of hot 20 per cent sodium hydroxide solution on silicon or ferro-silicon (an alloy of iron and silicon rich in silicon) :



The action of water on an alloy of lead and sodium, or on calcium hydride, has also been used :



Hydrogen is formed in some fermentation reactions, e.g. along with carbon dioxide in the industrial production of butyl alcohol ($\text{C}_4\text{H}_{10}\text{O}$) and acetone ($\text{C}_3\text{H}_6\text{O}$) by the anaerobic fermentation of starch :



Hydrogen is made in California by the thermal decomposition of hydrocarbons, especially methane (natural gas) : $\text{CH}_4 = \text{C} + 2\text{H}_2$. Gases from petroleum "cracking" are also used. The methane is also mixed with steam and heated : $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$.

Uses of hydrogen.—Hydrogen is used for filling balloons and airships, as it is the lightest gas known (normal density 0.08987 gm. per litre ;

density relative to air = 1 is 0.069) : coal gas is often used for balloons as it contains a good deal of hydrogen, and for airships hydrogen can be replaced by helium (which is twice as heavy) as the inflammability of hydrogen makes it dangerous for such a use. Hydrogen is used in the synthesis of ammonia, for "hardening" vegetable or animal oils by converting them into solid fats, for hydrogenating petroleum fractions, coal and other organic compounds, for lead "burning" (autogenous welding without solder, by a hydrogen flame), and in blowpipes.

Properties of hydrogen.—Hydrogen is a colourless gas which has no smell or taste when pure. It is sparingly soluble in water and the solubility is not much affected by change of temperature (p. 65). The solubility of hydrogen in alcohol is four times, and in petroleum three times, that in water. Hydrogen does not support respiration although it is not poisonous (unless it contains arsenic hydride as impurity). When breathed, mixed with some air, for a short time it weakens the voice and raises its pitch. Hydrogen is a better conductor of heat than other gases, its conductivity being about five times that of air. Its specific heat is also abnormally high, $c_p = 3.4$ at 0° . If a spiral of platinum wire, heated to redness by an electric current, is inserted into an inverted jar of hydrogen, the wire ceases to glow, on account of the increased loss of heat to the gas. At high temperatures dissociation of hydrogen molecules into atoms occurs: $H_2 \rightleftharpoons 2H$, the reaction absorbing a large amount of heat (about 100 k. cal. per gm. mol.).

The spectrum of hydrogen, obtained by an electrical discharge in a Geissler tube, contains four bright lines, due to atomic hydrogen and used in calibrating spectroscopes or refractometers : a red line H_α (Fraunhofer's C), 6562 Å.; a blue line, H_γ , 4340 Å.; a greenish-blue line, H_β (Fraunhofer's F), 4861 Å.; and an indigo line, H_δ , 4102 Å. (1 Ångstrom unit = Å. = 10^{-10} metre = 10^{-8} cm.)

Liquid and solid hydrogen.—Hydrogen is liquefied and solidified only with difficulty : the gas warms rather than cools by free expansion (p. 130) unless it has first been strongly cooled by liquid air. The liquid and solid are colourless and transparent. Olszewski in 1895 found that the slight heating effect produced by expansion through a valve at the ordinary temperature, changes on cooling to -80.5° at 113 atm. into a cooling effect. This inversion point makes it necessary in the liquefaction of hydrogen first to cool the gas strongly before expansion.

Liquid hydrogen was first obtained in bulk by Dewar in 1895, at the Royal Institution in London. By compressing hydrogen to 200 atm., cooling it to -200° , and expanding it through a valve, he obtained colourless liquid hydrogen, readily boiling off.

Liquid hydrogen may be prepared in the modification of Travers' apparatus devised by Nernst (Fig. 103). Compressed hydrogen enters through the copper coil *A* and passes through an extension *A'* of the coil immersed in liquid air in a large Dewar vessel. The cooled gas then passes through an extension of the coil *A''*, composed of two coils in parallel inside a small Dewar tube completely enclosed in a brass vessel *B*. At the end of this coil is an expansion valve *V* operated from outside. In the tube *A''* the previously cooled gas is liquefied by the cold expanded gas from the valve sweeping over the coil, and liquid hydrogen collects in the inner Dewar

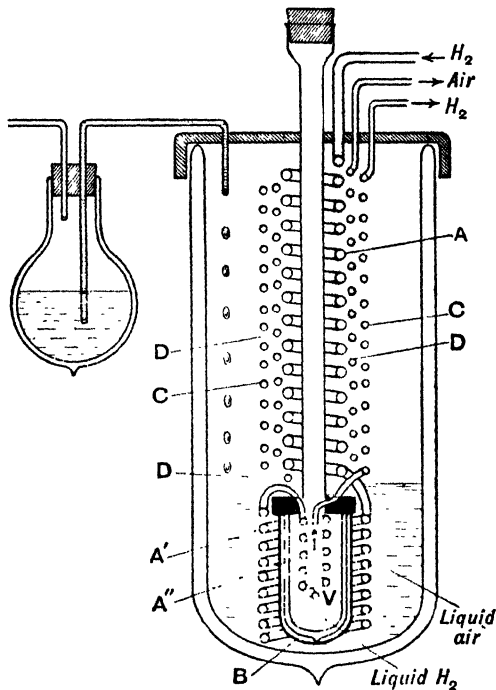


FIG. 103.—Preparation of liquid hydrogen.

vessel. The cold hydrogen gas passes out through a copper coil *C* wound in contact with the coil *A*, and takes heat from the incoming hydrogen in *A*. The liquid air boiling in the outer Dewar vessel gives off cold air which passes out through a copper coil *D*, wound between the two coils *A* and *C*, and also takes up heat from the incoming hydrogen. The brass vessel *B* is in two parts, screwed together, to permit of the inner Dewar tube being inserted. 300–400 ml. of liquid hydrogen are obtained per hour, with a gas velocity of 2–3 ml. per second, and the use of about 300 ml. of liquid air.

Liquid hydrogen is colourless and transparent, with the very small density of 0.07105 at its boiling point, -252.76° . By rapidly evapora-

ting the liquid under reduced pressure in a tube immersed in liquid hydrogen in a double Dewar vessel (Fig. 104), it freezes to a colourless transparent solid, or a white snow-like mass, m.pt. -259° . At the temperature of liquid hydrogen all other gases except helium and neon are frozen to solids which at the extreme cold show practically no vapour pressure.

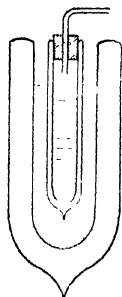


FIG. 104.—Preparation of solid hydrogen.

If a Geissler tube containing air is attached to a bulb containing charcoal, and the latter dipped into liquid hydrogen, the vacuum in the Geissler tube becomes so intense that no electrical discharge will pass even with a powerful coil.

If liquid hydrogen is poured into an ordinary test-tube, a white coating of ice at once covers the outside. From this, drops of liquid air are seen to fall.

Chemical properties of hydrogen.—Hydrogen forms compounds with a large number of elements, in many cases by direct combination: antimony, arsenic, barium, boron, bromine, calcium, carbon, chlorine, copper, fluorine, iodine, nickel, nitrogen, oxygen, palladium, phosphorus, potassium, selenium, silicon, sodium, strontium, sulphur, tellurium, and several rare metals, all form hydrides.

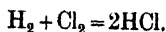
Hydrogen burns in oxygen or air to form water: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, but does not itself support combustion, as may be shown by passing a lighted taper into an inverted jar of hydrogen, when the taper is extinguished. Oxygen will also burn in hydrogen (p. 145). A mixture of hydrogen with air or oxygen explodes violently when kindled, provided either gas is not in too large excess.

Hydrogen and oxygen combine slowly at 180° , or in bright sunlight at the ordinary temperature. Explosion occurs with moist gases at 550° – 700° , but if the gases are exceedingly pure and dry they may be heated by an incandescent silver wire without explosion, though combination slowly occurs (Baker, 1902). The water produced appears to be so pure as to exert no catalytic influence on the reaction.

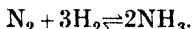
The mixture $2\text{H}_2 + \text{O}_2$ ignites at 526° on adiabatic compression, some combination occurring before the explosion itself (pre-flame period): the mixture $3\text{H}_2 + \text{O}_2$ ignites at 544° , and $\text{H}_2 + 4\text{O}_2$ at 478° , respectively (Dixon and Crofts, 1914). Thomas Thomson in 1817 gave 538° as the ignition temperature of hydrogen in air.

Hydrogen readily combines with fluorine and chlorine, less readily with bromine, iodine, sulphur, phosphorus, nitrogen, and carbon.

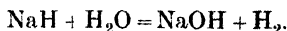
Hydrogen burns in chlorine and a mixture of hydrogen and chlorine explodes violently when kindled or exposed to bright sunlight:



Hydrogen combines with nitrogen on sparking or in presence of a catalyst, forming ammonia :



With a few metals, such as lithium, sodium, and calcium, it forms *hydrides*, such as NaH. These hydrides when pure are white salt-like compounds rapidly decomposed by water (KH explodes in air) :



The hydrogen in them behaves to some extent like a halogen or electro-negative element. On electrolysis of fused lithium hydride, the hydrogen is liberated at the *positive* electrode (Moers, 1920), not the negative as when water is electrolysed. Hydrogen is evolved at the anode in the electrolysis of a solution of calcium hydride CaH₂ in fused potassium and lithium chlorides (Bardwell, 1924).

Hydrogen, when passed over many heated metallic oxides (copper, iron, lead) reduces them to the metals : $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$.

The oxy-hydrogen and oxy-acetylene blowpipes.—When oxygen and hydrogen are supplied separately to a blowpipe jet consisting (Fig. 105)

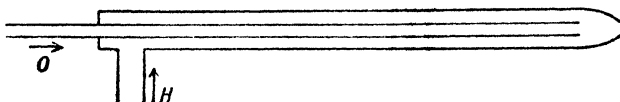
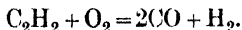


FIG. 105 —Oxy-hydrogen blowpipe

of two concentric metal tubes, the oxygen being inside, a blue, pointed, intensely hot flame is produced. Platinum wire readily melts in this flame, which has a temperature of about 2800°. Carbon monoxide instead of hydrogen gives a flame temperature of about 2600°. If the **oxy-hydrogen** (or oxy-coal gas) flame impinges on a small cylinder of quicklime, an intensely white light ("limelight") is given out by the infusible incandescent lime.

In the **oxy-acetylene** blowpipe acetylene gas takes the place of hydrogen or coal gas, and a hotter flame (3100°-3315°) is obtained. At this temperature, steam is practically completely dissociated, and the reaction is



The flame is therefore strongly reducing, which makes it suitable for welding metals. In cutting iron or steel a third inner tube is used and when the metal is heated by the flame to a high temperature, this inner oxygen jet is turned on. The iron itself then burns brilliantly, emitting showers of sparks, and rapidly fuses away. The oxygen jet is narrow, and a very clean cut is produced. Plates of steel 12 in. thick can be rapidly cut through in this way. Coal gas may also be used.

The acetylene and oxygen are used in the proportions 1.5 vols. of O₂ : 1 vol. of C₂H₂, the acetylene being either generated from calcium carbide and water *in situ*, or more conveniently used dissolved under pressure in acetone, soaked in a porous material contained in steel cylinders. (Compressed

acetylene gas is liable to explode spontaneously.) The porous material may be "kapok", seed-hairs in the pods of a tree (*Eriodendron anfractuosum*) growing in India and Java.

Atomic hydrogen.—Langmuir (1912) found that hydrogen at low pressure in contact with a tungsten wire heated by an electric current is dissociated to some extent into atoms: $H_2 \rightleftharpoons 2H$. This absorbs a large amount of energy, about 100 k. cal. per gram-molecule. The atomic hydrogen formed is chemically very active. Atomic hydrogen is formed when an electric arc between tungsten electrodes is allowed to

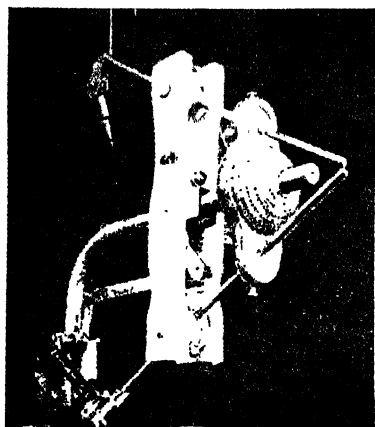


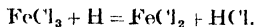
FIG. 106.—The atomic hydrogen blowpipe

Hydrogen gas issues from the central nozzle on the right and is dissociated in an electric arc between two tungsten rods nearly meeting in a V.

burn in hydrogen at atmospheric pressure (Fig. 106). The atomic hydrogen blown out of the arc by a jet of molecular hydrogen across the arc, forms an intensely hot flame, capable of melting tungsten (m. pt. 3400°). This flame obtains its heat from re-combination of hydrogen atoms to H_2 . It is suitable for melting and welding many metals. Iron can be melted without contamination with carbon, oxygen, or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys can be melted without fluxes and without surface oxidation. A feature of the flame is the great rapidity with which heat can be delivered to a surface which catalyses the reaction $2H = H_2$, and this is important in welding operations.

Nascent hydrogen.—Hydrogen being set free in a chemical reaction is often more reactive than hydrogen gas.

A little ferric chloride added to zinc and dilute sulphuric acid evolving hydrogen is rapidly reduced to a ferrous salt, as may be found by appropriate tests:

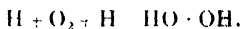


No such change is produced by bubbling gaseous hydrogen through the solution. Zinc and dilute sulphuric acid reduce potassium chlorate to potassium chloride.

It is usually supposed that the activity of such called **nascent** (new-born) hydrogen, in the act of liberation from its compounds, is due to the hydrogen being in the *atomic state*. Another theory is that the hydrogen is given off under great pressure: hydrogen gas under pressure reduces some metallic salts (*e.g.* $AgNO_3$ solution). The nature of the chemical action producing the hydrogen is of importance, because

potassium chlorate is not reduced by sodium amalgam, which reduces nitrites to hyponitrites. Zinc reduces nitrites to ammonia in presence of alkali. Zinc amalgam is often more effective than zinc alone, especially if a trace of copper salt is added, and "couples" of zinc with copper or iron are used for reduction. Hydrogen for reducing purposes may be liberated in alkaline solution by zinc or aluminium, and in neutral (aqueous) solution by copper-zinc couple or amalgamated aluminium. Gaseous hydrogen in presence of platinum or palladium black, or especially colloidal palladium (which takes up 2950 vols. of hydrogen), is a good reducing agent for solutions. At higher temperatures, hydrogen gas in presence of finely divided nickel is used to produce solid fats from liquid oils, the oil taking up hydrogen. Hydrogen liberated by electrolysis at a cathode, especially of amalgamated lead, is a reducing agent.

The atomic character of nascent hydrogen is made probable by the following experiment. A stream of oxygen is allowed to bubble through a liquid around a cathode at which hydrogen is being liberated. Hydrogen peroxide is formed. Langmuir found that atomic hydrogen unites directly with oxygen to form hydrogen peroxide :



The occlusion of hydrogen by metals.—Deville and Troost (1863) found that platinum and iron are permeable to hydrogen at a red heat, and concluded that "metals and alloys have a certain porosity." Graham (1866-69) showed that the penetration cannot be due to porosity since hydrogen is the only gas which passes through the metals.

Graham filled a platinum bulb with hydrogen and heated it in air. In half an hour 97 per cent of the hydrogen had passed out but no air entered, and a partial vacuum was produced in the tube. Five hundred ml. of hydrogen passed per sq. m. per minute through a platinum tube 1.1 mm. thick. Through a similar palladium tube the hydrogen began to escape at 100°; at a red heat 3993.2 ml. of gas passed out per sq. m. per minute. Palladium in a glass tube was exposed to hydrogen at 90°-97° for three hours, and allowed to cool in the gas for ninety minutes. When the tube was heated by a flame and the gas pumped off, the metal gave 643 times its volume of gas. Upwards of 500 vols. of gas were given out at 245° in a vacuum.

Graham at first said that : "the whole phenomenon appears to be consistent with the solution of liquid hydrogen in the metal . . . It may be allowed to speak of this as the power to occlude (to shut up) hydrogen, and the result as the occlusion of hydrogen by platinum." In 1869 he suggested that hydrogen was the vapour of an exceedingly volatile metal, *hydrogenium*. Solid hydrogen was later shown to be a transparent glassy solid with no metallic properties, but it is very probable that the hydrogen occluded in palladium is atomic and is behaving rather like a metal.

Palladium charged with hydrogen is a strong *reducing agent* : it

precipitates mercury from mercuric chloride solution, gives up hydrogen to chlorine and iodine in the dark, and reduces ferric to ferrous salts.

The occlusion of hydrogen by palladium is shown by immersing two strips of palladium foil in dilute sulphuric acid and using them as electrodes. Oxygen is evolved from the anode, but no gas from the cathode until the metal is charged with hydrogen. If the current is switched off, gas may come slowly from the cathode, showing that the metal was *supersaturated* with hydrogen. If the current is reversed, no gas comes from either electrode for a time. The oxygen is combining with the occluded hydrogen in one electrode, and hydrogen is being occluded in the other. After a time gas comes from both electrodes. The palladium strips bend, owing to the unequal expansion on absorption of hydrogen.

Troost and Hautefeuille (1874) pumped off hydrogen occluded in palladium, and measured the pressures during its removal at a given temperature. The first portions came off readily, but when 600 vols. of hydrogen were left to 1 vol. of palladium, the rest came off at a constant pressure, as water vapour from a crystal hydrate (p. 181). Hence these observers concluded that a definite *hydride of palladium* was present. Constant pressure intervals were observed at different temperatures.

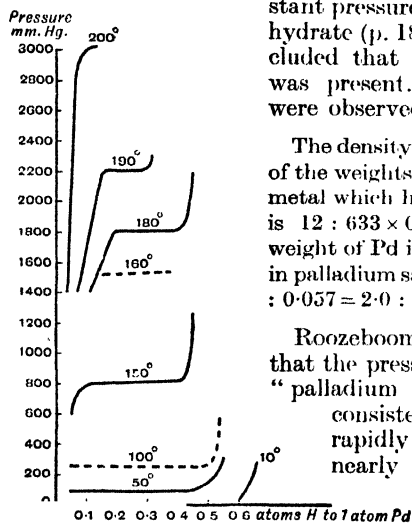


FIG. 107.—Palladium and hydrogen curves.

The density of palladium is 12, hence the ratio of the weights of palladium and hydrogen in the metal which has occluded 633 vols. of hydrogen is $12 : 633 \times 0.00009 = 12 : 0.057$. The atomic weight of Pd is 106, hence the ratio of the atoms in palladium saturated with hydrogen is $(12/106) : 0.057 = 2.0 : 1$, corresponding with Pd_2H .

Roozeboom and Hoitsema (1895) considered that the pressure curves in the dissociation of "palladium hydride" between 0° and 190° consisted of *three* parts (Fig. 107): two rapidly ascending parts joined by a nearly horizontal but slowly rising middle portion. At higher temperatures the flat part became shorter. The dotted curves give the results of Troost and Hautefeuille.

The shapes of the curves were thought to speak against a definite compound; with certain reservations Roozeboom and Hoitsema thought they indicated the formation of *two solid solutions*. The flat part, where the pressure is practically constant, shows that *two solid phases* must be present; since the pressure depends only on temperature, the phase rule gives $F=1$, $C=2$, $\therefore P=3$, i.e. gas + 2 solids.

Roozeboom and Hoitsema said their hydrogen contained a little nitrogen, which would explain the upward slope of the flat part of the curves, and they did not consider their experiments decisive enough.

Holt, Edgar, and Firth (1913) concluded that hydrogen exists partly as a condensed layer on the surface, and partly dissolved inside the metal, and is not uniformly distributed.

They found that palladium is normally inactive but becomes active as a result of : (a) oxidation by heating in air and reduction of the oxide film in hydrogen ; (b) heating to 400° in hydrogen, followed by cooling in the gas ; (c) heating to 400° *in vacuo*, when the hydrogen must be admitted as soon as cold, as the metal soon loses its activity. In all cases heating is necessary for activation. The absorption of gas is rapid at first, then becomes increasingly slower. The rate of diffusion of hydrogen through palladium 0.3 mm. thick was 3288 ml. per sq. m. per minute at 200° , and 5570 ml. at 476° .

By pumping out a palladium tube saturated with hydrogen and surrounded with the gas, the pressure inside was reduced to zero at the ordinary temperature, whilst the pressure on the other side was 10.4 mm. At 140° , with two pumps working equally on both sides, the outer surface of the tube lost 208 ml. of gas, and the inside only 12 ml. The hydrogen is not uniformly distributed through the metal. The surface layer is easily removed by pumping ; the gas inside is much more firmly held.

Gillespie and Hall (1926) took precautions to obtain states of true equilibrium, using very finely divided palladium and special heat treatment. They obtained perfectly horizontal isotherms (Fig. 108) and found evidence of two immiscible solid solutions, but at 80° , 160° and 180° , the one richer in hydrogen had practically the composition of a palladium hydride Pd_2H , which may be regarded as a definite compound separating nearly pure at higher temperatures, but at lower temperatures dissolving increasing amounts of hydrogen.

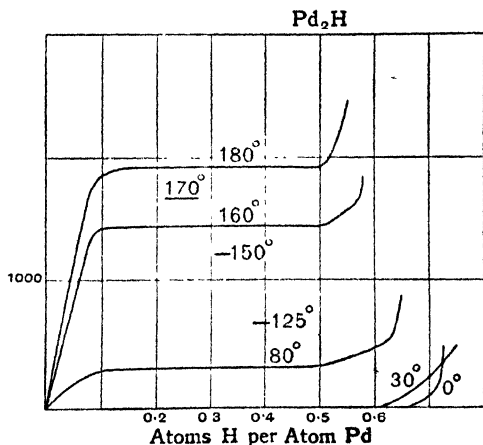


FIG. 108 — Gillespie and Hall's results.

Gillespie and Galstaun (1936) repeated the experiments over a wider range of temperatures and concluded that there are vertical steps of the boundary curves on both sides of the flat portions ; these correspond with the compositions Pd_5H and Pd_4H on one side, and Pd_3H and Pd_2H on the other.

Most finely-divided metals absorb small quantities of hydrogen, and metals prepared by electrolysis sometimes contain occluded hydrogen.

Catalytic combustion.—Although oxygen and hydrogen gases do not react at the ordinary temperature, a jet of hydrogen directed on a little

platinum sponge is inflamed. The same effect is produced by a bundle of perfectly clean fine platinum wires; these become red-hot and kindle the hydrogen (Döbereiner, 1823). The effect is not shown by other metals such as iron or copper, and the platinum exerts a specific *catalytic action*.

Döbereiner's lamp (Fig. 109) is a small hydrogen generator, consisting of a glass tube immersed in dilute sulphuric acid, with a stopcock and jet at the top. A piece of zinc hangs inside the tube, and the hydrogen generated displaces the acid until it is no longer in contact with the zinc, when action ceases. Opposite the jet is a sponge of fine platinum wire enclosed in a brass tube, and when the tap is opened the stream of hydrogen ignites. The activity of the platinum falls off, but it may be renewed by boiling the metal in nitric acid, when impurities from the hydrogen which cause the loss of activity are removed.

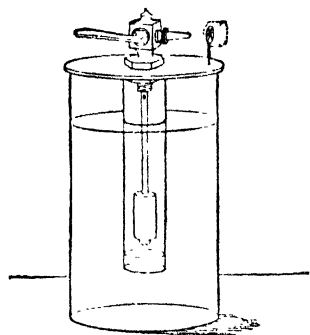


FIG. 109. Döbereiner's lamp.

Faraday (1833) observed that the combination of a mixture of hydrogen and oxygen is brought about by a piece of *clean* platinum foil—in some cases the gas explodes. There are two theories to account for this catalytic activity of platinum:

(1) Faraday considered that both gases form a *condensed film* on the metal as a result of surface-forces (*adsorption*). Under high pressure in this film the gases react. It is known that pressure may increase the activity of gases: Beketoff found that hydrogen gas under 100 atm. pressure displaces silver and mercury from solutions of their salts.

(2) De la Rive (1838) believed that *chemical compounds* are formed as layers on the metal. These unstable oxides react with hydrogen in a cyclic manner, the metal being alternately oxidised and reduced: $2\text{Pt} + \text{O}_2 = 2\text{PtO}$; $\text{PtO} + \text{H}_2 = \text{Pt} + \text{H}_2\text{O}$.

According to Faraday, platinum does not catalyse the union of hydrogen and chlorine. He found that the catalytic activity of a clean platinum surface was arrested when a small quantity of carbon monoxide was added to the mixture of hydrogen and oxygen, but the metal recovered its activity when brought into a gas mixture free from carbon monoxide. Traces of hydrogen sulphide in the gas "poisoned" the platinum so that it did not become active until boiled in concentrated sulphuric acid.

Graham in 1868 suggested that gas films formed by adsorption on metals might contain the gas molecules *orientated* in a particular direction, so that the same part of the molecule would always be in contact with the metal, and the other part exposed as a film to the gas space.

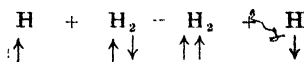
Langmuir showed that the adsorbed layer is unimolecular and is generally orientated, and that "poisoning" is due to the formation of films of molecules which prevent adsorption of other gases capable of reacting on a clean surface. In some cases (*e.g.* with carbon monoxide) the film may

evaporate again in a pure gas. Langmuir supposed that the adsorbed molecules are held by attractive forces analogous to chemical affinity, which originate in atoms of metal lying on the surface, and having uncompensated attractions. The metal atoms inside have no residual attractions since they are completely surrounded by other atoms. He regarded a metal surface as like a chess-board, the black spaces being metal atoms and the white spaces the spaces between the atoms. Molecules of gas are held by the spaces occupied by metal atoms. The catalytic action may take place by interaction between molecules or atoms held on adjacent surface atoms of metal, or between an adsorbed film and the atoms of the solid, or directly as a result of a collision between a gas molecule and a molecule or atom held on the surface. Reaction between hydrogen and oxygen occurs between adjacent adsorbed atoms, that between carbon monoxide and oxygen between oxygen atoms, formed from adsorbed oxygen molecules, and colliding carbon monoxide molecules. The products of reaction then evaporate from the surface. In the adsorption of gases on salt crystals, Haber (1914) considered that the molecules are held by electrical forces from the positive and negative ions of the salt in the surface of the crystal.

Orthohydrogen and parahydrogen molecules.—The hydrogen *atom* is supposed to consist of a very small positively charged nucleus called a *proton*, having practically all the mass of the atom, and a negatively charged electron at a relatively large distance from the nucleus. Both the proton and the electron have a property which can be described as a *spin* about an axis, rather like the rotation of the earth about its axis. A hydrogen molecule is formed from two atoms by two electrons of *opposite spins* pairing, and the two electrons in the molecule always have opposite spins. The two protons, however, may have their spins either in the same sense or in opposite senses, and two different kinds of hydrogen *molecule* result: the one in which the proton spins are in the same sense ("parallel") is called **orthohydrogen**, the one in which the proton spins are in opposite senses ("antiparallel") is called **parahydrogen**.

It was shown by Dennison (1927) that the curves representing the specific heat of hydrogen at low temperatures, which previously offered great theoretical difficulties, could be explained on the assumption that ordinary hydrogen is a mixture of these two kinds of molecules in the ratio of 3 to 1. Evidence of the existence of these in liquid hydrogen was found by an optical method by McLennan and McLeod early in 1929. In 1929, Bonhoeffer and Harteck found that when ordinary hydrogen is cooled and compressed, conversion of ortho- into parahydrogen occurs. On adsorbing ordinary hydrogen on charcoal at the temperature of liquid hydrogen, there is practically complete catalytic conversion into parahydrogen, which may be pumped off as gas. It has been shown that parahydrogen has a slightly lower boiling point than normal hydrogen.

By mixing parahydrogen (opposite spins) with atomic hydrogen (produced by an electric discharge in hydrogen), it is slowly converted into orthohydrogen (parallel spins):



Although pure parahydrogen can be obtained, pure orthohydrogen is not known, the maximum concentration obtainable being the 3 : 1 mixture in normal hydrogen. The specific heats and thermal conductivities of ortho- and parahydrogen are notably different.

Deuterium.—As a result of a supposed discrepancy between the chemical and mass spectrograph atomic weights of hydrogen, Birge and Menzel in 1931 suggested that ordinary hydrogen contains a small amount of a heavier isotope of atomic mass 2, and this was recognised spectroscopically in 1931 by Urey, Brickwedde, and Murphy, who called it *deuterium*, D. The enrichment of ordinary water in "heavy water" or deuterium oxide D_2O by prolonged electrolysis was effected in 1932 by Washburn and Urey, and in 1933 G. N. Lewis and Macdonald prepared nearly pure deuterium oxide and investigated its properties. Ordinary hydrogen contains about 1 part of deuterium to 6900 of "light hydrogen" (*protium*), and ordinary water contains a corresponding amount of D_2O . The ratio H : D varies very slightly in waters from different sources, the D_2O content being measured by small differences in density.

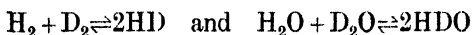
The principal method of enrichment of water in deuterium oxide is electrolysis: the light hydrogen is preferentially evolved, probably owing to the different overvoltages (p. 242) of the two hydrogens, and by prolonged electrolysis (the later fractions of evolved hydrogen, rich in deuterium, being burnt and returned to the cell) pure D_2O can finally be obtained. It is made commercially in Norway, and then contains about 0.38 per cent of $D_2^{18}O$ (containing heavy oxygen). Other methods of separation are of little practical interest, although fractional distillation is not without promise.

From deuterium oxide, gaseous deuterium D_2 is obtained by dropping the liquid on sodium: $2D_2O + 2Na = 2NaOD + D_2$, or (with less loss) by electrolysis of deuterium oxide in which phosphorus pentoxide has been dissolved. Some physical properties of "normal" hydrogen and deuterium, and of "normal" water and deuterium oxide, are given below.

	H_2	D_2	H_2O	D_2O
Density D_{25}^{25} - -	—	—	1.00000	1.10764
Temperature of maximum density - -	—	—	3.98° C.	11.23° C.
Boiling pt. - -	- 20.38° Abs.	23.50° Abs.	100° C.	101.42° C.
Freezing pt. - -	- 13.95° Abs.	18.65° Abs.	0° C.	3.802° C.
Triple pt. - -	- 13.92° Abs.	18.58° Abs.	0.0077° C.	3.809° C.

The D_2 molecule, like the H_2 molecule, exists in ortho- and para- forms, the equilibrium mixture at room temperature being 2 ortho- to 1 para-. At low temperatures it is almost all ortho (cf. H_2). The D_2 content of hydrogen gas may be found from the thermal conductivity or (below 1 per cent) by the mass spectrograph.

In mixtures of H_2 and D_2 , and of H_2O and D_2O , *exchange reactions* of H and D atoms occur and hence, owing to the reactions :



the molecules HD and HDO are also present. Exchange reactions occur between many hydrogen and deuterium compounds.

Every hydrogen compound could have a corresponding deuterium compound, and many have been prepared. The acid DCl is formed from the elements, and DF by the reaction $D_2 + 2AgF = 2Ag + 2DF$ at 110° . "Heavy ammonia" ND_3 is formed from D_2O and Mg_3N_2 and combines with many salts. Deuteromethane CD_4 is obtained from D_2O and Al_4C_3 , and deuteriacetylene C_2D_2 from D_2O and CaC_2 . The acids DNO_3 , D_2SO_4 and D_3PO_4 are formed by dissolving the anhydrides in D_2O . Association (*e.g.* of DF) is greater with deuterium compounds than with the corresponding hydrogen compounds (*e.g.* HF). The crystal hydrate $CuSO_4 \cdot 5D_2O$ is greener in colour than $CuSO_4 \cdot 5H_2O$. The dissociation pressures of deuterates (compounds of D_2O) and deuterammines (compounds of ND_3) with salts are somewhat smaller at a given temperature than those of corresponding hydrates and amines (compounds of NH_3).

Tritium.—A third isotope of hydrogen of mass 3, viz. 3H or tritium T, is formed artificially by the collision of deuterium nuclei (p. 407): $^2D + ^2D = ^3T + ^1H$. It is radioactive, emitting β -rays.

CHAPTER XIII

WATER AND HYDROGEN PEROXIDE

The physical properties of water.—Water exists as solid (ice), liquid (water), and vapour (steam). There are several varieties of ice.

Liquid water has a faint blue colour (liquid oxygen is blue) seen when light passes through a tube of water 2 m. long, closed at the ends with pieces of plate glass. Ice shows the same colour in large masses, as in crevices of glaciers or icefloes. The deep blue colour of some clear lakes appears to be due to light scattered from fine particles of solid matter in suspension.

Liquid water is only slightly compressible : between 1 and 25 atm. an increase of pressure of 1 atm. reduces the volume by only 5 parts in 100,000. The expansion of water by heat is peculiar. From 0° to 3·98° the liquid *contracts*, above 3·98° it expands, and at 3·98° water has its *maximum density*. Owing to this, exposed water freezes on the surface ; the water sinks as it reaches 3·98° and forms a heavier layer below the crust of ice, through which heat passes only slowly.

The volume of 1 kgm. of water at 4° weighed *in vacuo* is defined as the **standard litre** ; it occupies 1000 ml. or 1000·028 cm.³. The volume of 1 kgm. of water at 15° weighed *in air* is **Mohr's litre** = 1001·98 cm.³

The density of ice at 0° is 0·9168 ; it floats on water, which expands on freezing. The liquid may be supercooled to about -20°. Cast-iron bottles filled with water and closed with screw plugs burst when immersed in a freezing mixture.

The **densities** of water, referred to the mass in grams of one-thousandth of a standard litre (1 ml.) at 4° as unity, are :

- 5°	0·99930	8°	0·999808	100°	0·9584
0°	0·99987	10°	0·99973	150°	0·9173
4°	1·00000	20°	0·99823	250°	0·794

The amount of heat required to raise the temperature of 1 gm. of water from 14½° to 15½° is called the **gram calorie** (g. cal.). The corresponding amount for 1 kilogram of water is the **kilogram calorie**, 1 k. cal. = 1000 g. cal. The number of units of work spent in generating 1 g. cal. by stirring water is the **mechanical equivalent of heat**, $4·185 \times 10^7$ ergs per 15° g. cal. The number of g. cal. required to raise the temperature of 1 gram of a substance through 1° under specified conditions is the **specific heat** ; the specific heat of ice is 0·502.

Ice is converted into water with a considerable absorption of heat, although the temperature remains constant at 0°. This heat, 79·74 g. cal. per gram of ice, is the **latent heat of fusion** of ice. Water at its

boiling point is converted into steam with a large absorption of heat, 539.1 g. cal. for 1 gm., called the latent heat of evaporation of water. In the reverse changes exactly the same quantities of heat are evolved.

Drops of water floating in oil are readily heated much above 100° without vaporising, and are then said to be superheated.

The vapour density of water just above the boiling point is slightly greater than corresponds with the formula H_2O . When this is corrected for deviations from Boyle's laws the results show that steam consists almost entirely of H_2O molecules. The properties of liquid water, its high surface tension, high dielectric constant, great tendency to promote ionisation of dissolved electrolytes, high boiling point as compared with hydrogen sulphide H_2S , the expansion on solidification, and the existence of a maximum density above the freezing-point, all show that water is an abnormal liquid (p. 135).

The equilibria between the *phases of water* are shown diagrammatically in Fig. 110. AL is the vapour pressure curve of liquid water, ending at the critical point L. Since increase of pressure at a given temperature condenses vapour to liquid, the liquid and vapour fields are as shown. SA is the vapour pressure curve of ice: it has a greater slope (exaggerated in the figure) at the triple point A than that of water AL. At A, ice water and vapour are in equilibrium. AB is the melting curve of ice at different pressures; since the m.pt. is lowered by increase of pressure, AB slopes to the left. The dotted curve represents supercooled water, which is a *metastable state*, since in presence of ice the liquid would solidify. The vapour pressures of metastable states are always greater than those of stable states at equal temperatures.

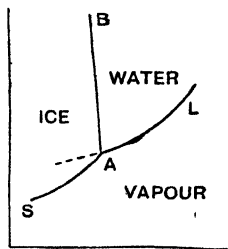


Fig. 110.—Phase diagram for water.

For carbon dioxide the point A lies at about 5 atm. pressure, so that under atmospheric pressure solid carbon dioxide ("dry ice") passes directly into gas without melting.

At higher pressures several different *forms of ice* appear, so that the upper part of the curve AB is complicated.

Ordinary ice, ice I, is in equilibrium with water vapour and liquid water at $+0.0077^{\circ}$ C. under a pressure of 4.579 mm. It is always produced when water crystallises spontaneously under pressures less than 2,500 kgm./cm.² Above this pressure ice III or ice II forms; between pressures of 3,500 and 6,300 kgm./cm.² ice II or ice V is produced, according to the temperature; under higher pressures ice VI is formed. Ice II ($d=1.03$) cannot exist in equilibrium with liquid water. Ice I, ice II and ice III ($d=1.04$) have a triple point at -34.7° C. and 2,170 kgm./cm.²; ice II, ice III and ice V ($d=1.09$) are in equilibrium at -24.3° C. and 3,510 kgm./cm.² The existence of ice IV is doubtful; ice VI ($d=1.06$) is stable only at temperatures above 0° C. Ice II and ice III differ in space lattice only.

Ice crystallises in the hexagonal (six-sided) system (Fig. 111). The bubbles in ice are composed of air dissolved in the water and liberated on freezing. In making clear ice, freezing is carried out slowly and with agitation, so that air bubbles can escape.

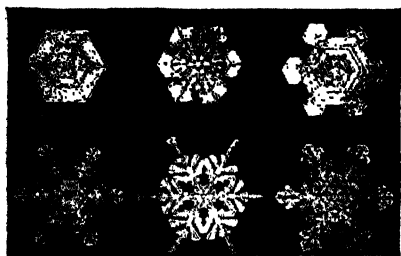


FIG. 111.—Snow crystals.

Hydrates.—Definite solid compounds of salts with water are called hydrates. A salt in the dry condition, free from water, is called an *anhydrous* salt. Many anhydrous salts differ in colour and crystalline form from the hydrates. If an anhydrous salt can exist in contact with a saturated solution, its solubility is different from that of the hydrate (p. 67). White anhydrous copper sulphate becomes blue if water is poured on it, and heat is evolved. On cooling a hot solution in water, deep blue crystals of the hydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (*blue vitriol*) separate. If exposed to dry air in a desiccator over sulphuric acid, they fall to a nearly white powder of the monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, which becomes blue when moistened with water.

Some crystal hydrates lose water and fall to powder on exposure to the atmosphere. This change is called *efflorescence* and shows that there must be a pressure of water vapour over the salt: this is confirmed by passing a crystal of the salt above the mercury in a barometer tube, when the mercury falls slightly. The vapour pressure is constant at a given temperature and increases with the temperature.

The system has two components, anhydrous salt and water. Since the vapour pressure depends only on temperature, there is one degree of freedom; hence the phase rule, $P + F - C + 2$, shows that the number of phases is $2 + 2 - 1 = 3$. These are water vapour and *two* solids. One solid is the original hydrate, the second is either anhydrous salt as with Glauber's salt: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$, or a lower hydrate as with copper sulphate: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} = \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$.

When the vapour pressure above the hydrated salt at the ordinary temperature is greater than the partial pressure of water in the atmosphere, the salt loses water on exposure and effloresces. If the vapour pressure over the salt is not greatly different from that of atmospheric moisture, the crystals will be stable on exposure. If the vapour pressure over the hydrate is very small, the salt may absorb moisture from the air. Calcium chloride, used for drying gases, absorbs moisture forming $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, with a small vapour pressure.

The name efflorescence first denoted the "creeping" of solutions of salts in open vessels, with the formation of a loose deposit. This is caused by the formation of crystals on the walls at the surface of the liquid, which then

risers by capillary action between the crystals or between these and the wall. More crystals are formed above, and in some cases the solid reaches the top of the vessel, when the solution may siphon over and creep down the outside. This occurs with sal ammoniac solutions in Leclanché cells and may be prevented by greasing the upper part of the jar.

Vapour pressures of hydrates.—A mechanical mixture of liquid water with an insoluble solid has a vapour pressure equal to that of pure water.

A hydrate containing hygroscopic moisture in excess of its combined amount has a vapour pressure equal to that of its saturated solution. If water is removed as vapour until the excess has been lost the pressure will drop to that of the solid hydrate, say $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and the pressure falls to *A* (Fig. 112). Dissociation of this hydrate begins: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}$, and the phase rule shows that the system of two solid hydrates, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, and vapour has a definite pressure. Continued abstraction of water converts all the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, and the pressure falls to a lower value *C*.

Dissociation into $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ now begins: $\text{CuSO}_4 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot \text{H}_2\text{O} + 2\text{H}_2\text{O}$. This hydrate has a very small vapour pressure, but emits water in a desiccator over phosphorus pentoxide to form anhydrous salt. When all the trihydrate is converted into monohydrate, the pressure falls to a low value *B*, and remains at this until all the water is removed: $\text{CuSO}_4 \cdot \text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 + \text{H}_2\text{O}$. It then falls to zero over the anhydrous salt. By analysing the solid when drops of pressure occur, say at *C*, the composition of the hydrates may be found.

Natural waters.—Natural water contains various impurities present in amounts varying with the source of the water. The following division of natural waters is convenient: (1) rain water, (2) river water, (3) spring, or deep well, water, (4) sea water, and (5) mineral waters.

Impurities in natural waters are of two kinds: (1) *suspended*, both mineral and organic; (2) *dissolved*, both solids (mineral and organic) and gases. The amounts of impurity vary a good deal with the source of the water.

Rain water contains impurities, especially near or in towns where coal is burnt. Dissolved atmospheric gases (oxygen, nitrogen, carbon dioxide), and sodium chloride from sea-spray carried inland by winds, are always present. Nitrous and nitric acids produced by electrical discharges (lightning) are usually present as ammonium nitrite and nitrate, and there is sometimes free ammonia. In towns sulphuric acid from the combustion of iron pyrites FeS_2 in coal is present, and

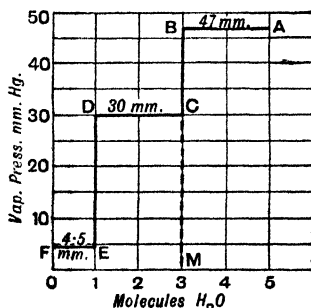
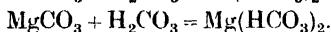
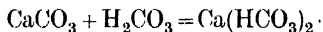


FIG. 112.—Vapour pressure curves for hydrates at 50° .

suspended impurities, chiefly soot from fuel smoke. The free sulphuric acid may be neutralised by lime-water, or by allowing the water to stand over limestone. Melted snow contains similar impurities.

River water is rain water which has percolated through the surface soil and contains suspended and dissolved impurities from the soil. Some spring water may be mixed with it. The suspended matter is partly clay and partly organic (vegetable) matter. The dissolved matter consists mainly of calcium and magnesium salts. The atmospheric carbon dioxide dissolved in rain, and that taken up from decaying vegetable matter in the soil, forms carbonic acid : $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$. This is a very weak acid, but it dissolves calcium carbonate from limestone or chalk over which the water flows or that present in the soil, and also magnesium carbonate, to form soluble calcium and magnesium bicarbonates :



If calcium sulphate (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is present in the soil or rocks it dissolves, and sometimes the water may contain calcium chloride CaCl_2 , and magnesium sulphate MgSO_4 and chloride MgCl_2 , from the soil. All these salts produce *hardness* in water.

River water flowing over cultivated land also contains sodium chloride, and ammonium salts and nitrites and nitrates formed by bacterial action on nitrogenous organic matter of vegetable and animal origin.

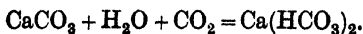
The purity of the water depends on the nature of the soil. Thames water flowing over soil rich in limestone contains about 157 milligrams of calcium carbonate per litre. Trent water flowing over soil containing gypsum contains 300 milligrams of calcium sulphate per litre. The waters of the Dee and Don draining the Aberdeen granite area contain only traces of dissolved calcium salts, and Glasgow water from Loch Katrine contains only 30 milligrams of total solid matter per litre. Bala Lake water is also very soft.

Spring or deep well water differs from river water only in having undergone filtration through porous strata. In this way suspended matter may be largely removed, leaving the water clear. The organic matter and nitrites, if present, may have been more or less oxidised to nitrates, but the dissolved mineral matter usually increases.

Temporarily hard water.—The formation of calcium bicarbonate from calcium carbonate and carbonic acid is shown by passing a slow current of washed carbon dioxide into clear lime water (a solution of calcium hydroxide). A white precipitate of calcium carbonate is first formed :

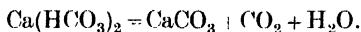


As the carbon dioxide continues to pass, this precipitate dissolves and a clear solution of calcium bicarbonate is formed :

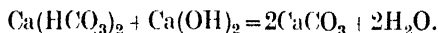


The calcium carbonate dissolved as bicarbonate may be precipitated in two ways :

(1) By boiling part of the solution in a flask, when carbon dioxide is evolved and a white precipitate of calcium carbonate is formed :



(2) By adding an equal volume of the lime water to another portion of the solution, when calcium carbonate (solubility 0.013 gm. per litre) is precipitated :



Hard water containing calcium bicarbonate deposits a "fur" or "scale" of calcium carbonate (often coloured brown by iron oxide and organic matter) in kettles or boilers. Such water, which is softened by boiling, is called *temporarily hard water*. It may be softened for use by adding just enough lime (calcium hydroxide) or lime water to precipitate the calcium bicarbonate and then filtering from the calcium carbonate. This is called **Clark's process**. Some calcium carbonate may remain in supersaturated solution.

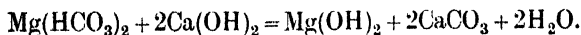
Waters containing dissolved calcium bicarbonate when they fall in drops from the roofs of caves lose carbon dioxide and deposit calcium carbonate in the form of *stalactites*. The drops falling on the floor cause a *stalagmite* of calcium carbonate to grow upwards to meet the stalactite (Fig. 113). Stalactites formed under



FIG. 113 -Stalactites and stalagmites.

brickwork arches come from the calcium carbonate in the mortar, which is dissolved by carbon dioxide in rain.

Water containing magnesium bicarbonate $\text{Mg}(\text{HCO}_3)_2$ is not softened by boiling, since magnesium carbonate MgCO_3 is appreciably soluble in water (0.84 gm. per litre). In this case enough lime must be added in **Clark's process** to precipitate the sparingly soluble magnesium hydroxide (solubility 0.01 gm. per litre) as well as any calcium bicarbonate present :



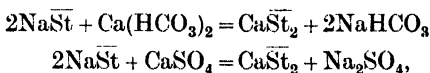
Ferrous carbonate FeCO_3 is present in some soils and also dissolves in water containing carbon dioxide, forming ferrous bicarbonate $\text{Fe}(\text{HCO}_3)_2$.

On boiling or exposure to air, a reddish-brown precipitate of ferric hydroxide $\text{Fe}(\text{OH})_3$ ("rust") is thrown down, since ferrous bicarbonate is easily oxidised by atmospheric oxygen :



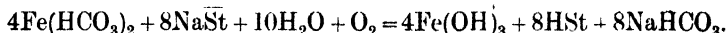
Water containing iron stimulates the growth of a thread-like organism *Crenothrix*, which gives the water a bad taste and causes a precipitate of ferric hydroxide which may stop up pipes. The ferrous bicarbonate may be removed by aeration, when it precipitates as ferric hydroxide.

All kinds of hard water cause waste of soap, since they react with the soap, which consists of the sodium salts of fatty acids such as stearic acid, and form a slimy precipitate or scum of the calcium and magnesium salts, which also carry some soap down with them :



where $\overline{\text{St}} = \text{C}_{17}\text{H}_{35}\text{COO}^-$ is the stearate radical.

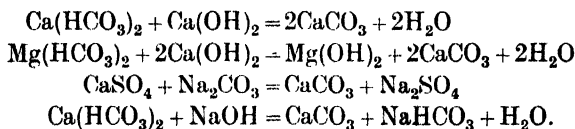
If ferrous bicarbonate is present, brown ferric hydroxide is precipitated, causing "iron mould" on fabrics :



The calcium and magnesium salts in hard water cause a larger waste of soap than corresponds with the production of the calcium and magnesium salts of the fatty acids. About 0.17 lb. of soap is required for 100 gallons of water containing 1 grain of CaCO_3 per gallon, instead of 0.075 lb. (theoretical). The slimy precipitate of calcium salts carries down some soap and renders it useless. It also adheres tenaciously to the skin or fabric, and interferes with washing. The hard water does not acquire the smooth feeling characteristic of a soft water (free from dissolved calcium and magnesium salts), which is intensified by traces of alkali from the excess of soap, but retains its harsh feeling until excess of the soap has been added.

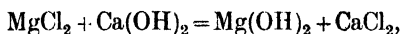
Permanently hard water.—Water containing dissolved calcium sulphate (solubility 2 gm. per litre) is not softened by boiling. The hardness due to calcium sulphate, and also to magnesium sulphate and calcium and magnesium chlorides which are sometimes present, is called *permanent* hardness. The water may have temporary hardness as well. Such waters when evaporated in kettles or boilers deposit calcium sulphate CaSO_4 as a very hard crystalline "fur" or scale. This is not due to a chemical change but to loss of water by evaporation until the saturation point of the dissolved calcium sulphate is reached. (The scale is said to be CaSO_4 , not $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.) The solubility also decreases with rise in temperature and at the higher temperatures in steam boilers CaSO_4 is almost insoluble. Such waters cause waste of soap in laundry work for the same reason as temporarily hard water, i.e. they precipitate soap as calcium and magnesium salts.

Water softening.—Water for domestic and industrial purposes may have to be softened if it is too hard as it comes from the source. The *temporary hardness* is removed by Clark's process (p. 183). For industrial purposes (boilers and laundries) the *temporary and permanent hardness* are both removed by adding lime and sodium carbonate, and sometimes sodium hydroxide :

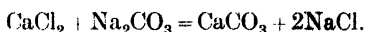


Calcium carbonate is much less soluble than calcium sulphate and is precipitated.

If magnesium chloride is present, the reaction with lime is :

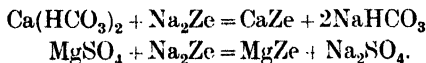


and the calcium chloride must then be precipitated by sodium carbonate :

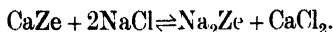


The process of water softening now mostly used is the "base-exchange" or "zeolite" process. In this the hard water is percolated through granules of a material such as *Permutit*, which is a trade name for an artificial sodium aluminium silicate allied to the natural zeolites. Commercial zeolites are also made from natural greensand (glauconite).

The zeolite may be formulated as Na_2Ze , where Ze stands for the "zeolite radical"; this is often given the composition $\text{Ze} = \text{Al}_2\text{Si}_2\text{O}_7$ or $\text{Al}_2\text{H}_4\text{Si}_3\text{O}_{12}$, but the commercial zeolites contain more silica and approximate to $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_n$, where n varies from 5 to 13. The calcium and magnesium salts in the water react as follows :



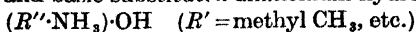
During use the zeolite loses its activity and it is regenerated by percolating with a concentrated solution of common salt, which displaces the calcium and magnesium from the zeolite and replaces these by sodium, so that the mass is ready for use again :



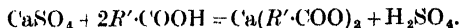
The reaction is reversible and in practice about $2\frac{1}{2}$ times the theoretical amount of salt is used.

A zeolite containing manganese dioxide oxidises dissolved iron and manganese salts, which are injurious in laundering as they form spots, and precipitates them as oxides. The mass is regenerated by percolating with permanganate solution.

In a newer process, separate synthetic rosins containing acidic carboxyl groups $R'\text{-COOH}$ and basic substituted ammonium hydroxide



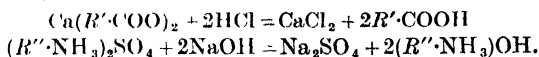
are used to remove both basic (Na, Ca, Mg) and acidic (HCO_3 , Cl, SO_4) radicals. The water is first passed over granules of the acidic resin, when basic radicals are removed and an acid is formed :



The acid is then removed by passing the water over the basic resin :



The resulting water may be as pure as distilled water. The resins are regenerated by percolating with acid and alkali solution, respectively :



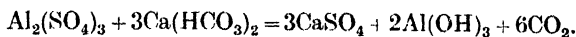
Water used in boilers may be softened by adding sodium hexa-metaphosphate (p. 584), or trisodium phosphate (p. 695), and in laundry work borax (p. 653) and sodium metasilicate (p. 694) are used.

The "hardness" of water is determined by adding from a burette to 100 ml. of the water a standard soap solution*, shaking after each addition until a lather is formed which lasts a minute. The soap solution is standardised and (after subtracting 1 ml. for the amount to produce a lather with 100 ml. of distilled water) the number of ml. used gives the *degree of hardness* in parts of CaCO_3 (so expressed whether temporary or permanent) per 100,000 of water. Another unit is grains per gallon, and this divided by 0.7 gives parts per 100,000. A soft water has a hardness not exceeding 10° , a medium hard water from 10° to 20° , a hard water from 20° to 30° , and a very hard water above 30° . Thames water has a mean hardness of 20° which is reduced to 5° after lime-softening.

The following analyses of river waters provide material for problems on water softening, the amounts being in parts per 100,000 :

	CaCO_3	CaSO_4	MgCO_3	NaCl	SiO_2	Organic matter
Thames - - -	14.4	4.5	1.8	2.6	0.8	3.4
Trent - - -	0.46	30.1	8.1	2.5	1.0	5.2
Dee (Aberdeen)	1.2	0.17	0.51	1.0	0.2	2.2
Dou ,,	3.2	0.2	1.5	1.8	0.75	4.3

Sterilising water.—For use for drinking purposes (*potable water*) the water must be filtered and also sterilised if it is likely to contain harmful bacteria. Filtration is carried out through beds of gravel and sand, which become covered with a layer of clay, algae, etc., which removes suspended matter and also many bacteria. If necessary a little aluminium sulphate may be added to clarify the water from finely suspended clay; alumina is precipitated and carries down suspended particles and also some bacteria :



The water is sterilised by adding bleaching powder solution, or chlorine gas, or a mixture of chlorine and ammonia (*chloramine process*)

* Dissolve 13 gm. of Castile soap shavings in 500 ml. of methylated spirit by heating on a water bath and add 500 ml. of distilled water. 1 ml. = 1 mgm. CaCO_3 .

—which is more effective than chlorine alone), or by bubbling ozonised air through the filtered water, or by exposure to ultraviolet light.

Action of water on lead.—Hardness in drinking water is not known to be injurious to health : the presence of bicarbonates gives the water a refreshing taste and prevents its action on lead pipes.

Very soft water containing dissolved air will dissolve lead and the action is greater in presence of *free* carbonic acid. The dissolved lead is poisonous. Lead is rapidly attacked by distilled or rain water in presence of air, forming lead hydroxide $Pb(OH)_2$, which is appreciably soluble or forms a colloidal solution. The action is due partly to dissolved oxygen, and partly to *free* carbonic acid. Hard water has much less action on lead than soft water, since the dissolved bicarbonate and sulphates form a protective coating of insoluble lead salts on the metal. Peaty water containing organic acids acts rapidly on lead (or zinc) unless neutralised by lime.

Two pieces of clean lead pipe are placed in two beakers containing distilled water and tap-water, respectively, the metal being only partly covered. Allow the beakers to stand for a few hours. The distilled water rapidly becomes turbid, whilst the tap-water (if hard) remains clear. Pour off the liquids, and add hydrogen sulphide water. Compare the brown or black colorations, due to lead sulphide. The water should not be filtered, as dissolved lead hydroxide is retained to some extent by filter-paper.

Mineral waters.—Natural waters containing special constituents not present (except in traces) in ordinary water are known as mineral waters. They are of several kinds :

- (1) **Acidulous waters** (*e.g.* Apollinaris and Seltzer, *i.e.* Selters) contain dissolved carbon dioxide and sometimes common salt. The carbon dioxide may be liberated with effervescence when the water is shaken or slightly warmed. Some acidulous waters contain sulphuric acid, from the oxidation of sulphur dioxide or iron pyrites.
- (2) **Alkaline waters** (*e.g.* Vichy water) contain sodium bicarbonate $NaHCO_3$, and sometimes lithium bicarbonate $LiHCO_3$, which are supposed to be beneficial in the treatment of gout.
- (3) **Bitter waters** contain various salts : *e.g.* Marienbad water (sodium sulphate), Epsom water (magnesium sulphate), Friedrichshall and Hunyadi-Janos waters (sodium and magnesium sulphates).
- (4) **Chalybeate or ferruginous waters** (*e.g.* Pyrmont water) contain ferrous bicarbonate. On exposure to air such water deposits brownish-red ferric hydroxide.
- (5) **Hepatic waters** (Latin *hepar*, liver) contain hydrogen sulphide H_2S and alkali sulphide, *e.g.* Na_2S . They smell of hydrogen sulphide, and on exposure to air deposit sulphur : $2H_2S + O_2 = 2H_2O + 2S$. Harrogate water is of this type.

(6) **Siliceous water** contains dissolved silica and alkali silicates. Such waters, *e.g.* of the geysers of Iceland, New Zealand, and Yellowstone Park (America), are usually almost boiling and deposit masses of siliceous sinter at the mouth of the geyser.

(7) **Iodine water** contains dissolved iodides and occurs at Woodhall Spa (Lincoln) and in Central Europe.

Hot-springs occur in various places, *e.g.* Buxton (28°) and Bath (47°). They contain dissolved gas, including helium, and traces of radium emanation.

Sea water contains dissolved salts, especially sodium chloride. An analysis of the water of the Irish Sea, in parts per 1000, is :

NaCl	KCl	MgCl ₂	MgBr ₂	MgSO ₄	CaSO ₄	CaCO ₃	MgI ₂
26.44	0.746	3.151	0.0705	2.066	1.332	0.0475	0.0025

Sea water behaves as a hard water since it contains calcium and magnesium salts and also because the common salt in it precipitates soap as such, or prevents it from forming a solution.

Pure Water.—For chemical purposes water is purified by distillation. If the intermediate portion of the distillate is collected in good glass bottles, previously steamed out to remove the alkaline layer from the glass, the water is very nearly pure. A copper vessel with a pure tin or a copper condenser without brazing is the best apparatus to use. Still purer water is obtained by destroying the nitrogenous organic matter (which gives traces of ammonia on distillation) by passing chlorine through boiling distilled water for half an hour. The chlorine is boiled out, pure potassium hydroxide and permanganate are added, and the water distilled, the first half being rejected and a quarter only of the remainder collected. The process is repeated with this fraction.

The combining volumes of hydrogen and oxygen.—Early experiments on the composition of water by volume are those of Cavendish (1781) who obtained the ratio H:O = 201 : 100, Gay-Lussac and Humboldt (1805) who found 199.89 : 100, and Bunsen, whose numerous determinations indicated an almost exact ratio of 2 : 1.

Accurate measurements of the combining volumes were made by Alexander Scott, whose experiments in 1887–9 and 1893 at first gave slightly varying ratios, from 199.4 : 100 to 200 : 100. The later experiments showed that this variation was due to a very thin film of grease carried over from the lubrication of the stopcocks into the eudiometer, which took up a little oxygen during the explosion, burning to carbon dioxide and steam. The apparatus (Fig. 114) consisted of a pipette *A* in which gas was measured and passed into a mixing container *H* over mercury. Pure oxygen was obtained by heating silver oxide, pure hydrogen by the action of steam on sodium. The mixed gas was exploded in portions by sparking in the eudiometer *J* and the residual gas measured in *A* and analysed. In this way the volume ratio hydrogen : oxygen = 2.00285 : 1 at S.T.P. was found. Moles (1925) recalculated Scott's value as 2.00302 : 1.

Burt and Edgar (1915) found as the average of 59 determinations, 200.288 : 100, agreeing with Scott's value to 3 parts in 200,000. The

special points of the research were: (1) very carefully purified gases were used; (2) the actual measurements were carried out at 0° and under 1 atm. pressure, so that temperature and pressure corrections were eliminated.

The hydrogen, prepared by the electrolysis of recrystallised barium hydroxide solution, was dried by phosphorus pentoxide and further purified: (i) by passing over charcoal cooled in liquid air which adsorbs oxygen and nitrogen but only a little hydrogen; (ii) by passing through a tube containing palladium black to convert oxygen to water, and then pumping the gas through the walls of a closed palladium tube heated electrically. The palladium tube was welded to a short platinum tube

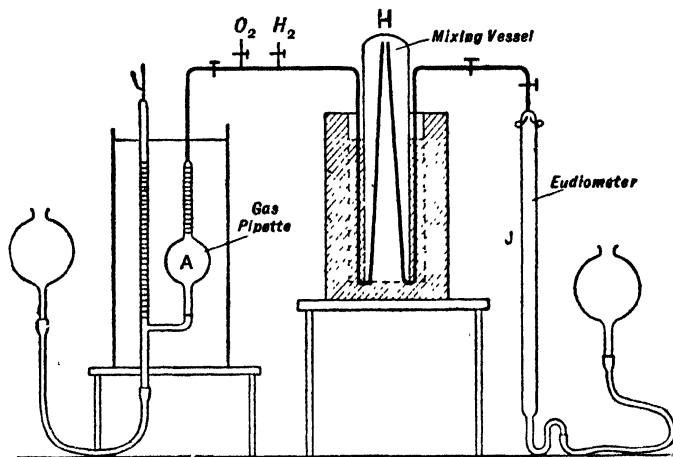


FIG. 114.—Scott's apparatus.

sealed into a glass tube. This was sealed inside a wider tube, and the palladium heated by a platinum spiral wound on a quartz cylinder slipped over it. The palladium was protected from mercury vapour from the pumps by plugs of gold wire sponge. The palladium was charged with hydrogen at 100° , 300 ml. of gas were pumped off at 180° and the metal was recharged with hydrogen at 100° .

The oxygen was prepared: (1) by the electrolysis of barium hydroxide solution, liquefaction in fresh liquid air, and fractionation; (2) by heating pure potassium permanganate in glass tubes and washing the gas (a) with concentrated potassium hydroxide solution, (b) with saturated barium hydroxide solution, (c) with very concentrated potassium hydroxide solution. The gas was then dried by sticks of potassium hydroxide, and phosphorus pentoxide, liquetied, and fractionated.

The apparatus (Fig. 115) consisted of a 300 ml. glass pipette *A* sealed to capillary tubes at each end. The lower capillary was expanded to a dead-space *B* of 1 ml. capacity, with a glass levelling-point. The upper capillary led to a 3-way tap *C*. The pressure of the gas in the bulb was equal to the vertical distance between the mercury surface in *B* and that in the upper

chamber *D*, also provided with a levelling point. *B* and *D* were kept at a constant distance apart by a stout glass rod sealed between them. The manometer head passed to a mercury pump. The T-piece *H* and the tap *J* formed a *volume adjuster*; the capacity of the pipette *A* could be varied within narrow limits by withdrawing mercury from *H*; this mercury could be weighed, and its volume thus accurately determined. The bulb *A* and

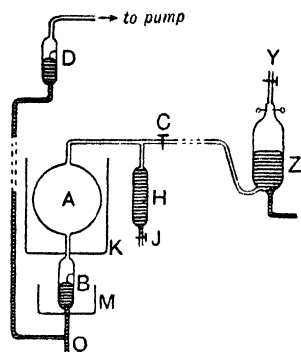


Fig. 115.—Burt and Edgar's apparatus.

upper part of the apparatus were enclosed in an ice-bath, the lower dead-space was surrounded by a small brine bath *M*. The mercury for displacing the gas was contained in a bulb below, and an air-catch *O* protected the pipette from air leaks through the rubber. The volume of the apparatus from *C* to the level of the glass point in the dead-space *B* was determined by weighing the contained mercury.

The gas was allowed to enter the pipette, displacing mercury through *O* until the mercury surfaces in the dead-space and manometer stood at the glass-points. Since there was a vacuum above the mercury in the manometer, the gas was measured under the pressure of this

mercury column, which was 1 atm. The tap admitting gas was then closed and the fine adjustment made by the volume adjuster *H*, by which small amounts of gas could be added to the pipette.

The gas was allowed to reach the temperature of the ice-bath, which took about three hours, and was then passed to the 1 litre explosion bulb *Z* by opening *C* and raising the mercury reservoir attached to *O*, mercury being displaced from *Z* through an air-trap to a reservoir. Two pipettes of hydrogen with a little excess, measured by the volume adjuster, were passed into *Z*. A pipette of oxygen was added in portions, firing the gas by an electric spark after each addition. The small residual volume of wet hydrogen was sparked for a few minutes. The explosion vessel was then cooled by a mixture of solid carbon dioxide and acetone to freeze the water, the pressure reduced, and the residual gas sucked off through a phosphorus pentoxide tube into a small pump, a spiral cooled in liquid air being interposed. The gas volume was measured as follows. The pipette *A* was filled with hydrogen and carefully levelled. The small volume of residual gas was then added and the pressure adjustment made by running a little mercury from the adjuster *J*. From the weight of this mercury the volume of the residual gas added to that in the bulb was calculated.

The weights of 1 litre of hydrogen and oxygen at S.T.P. according to Morley, are 0.089873 gm. and 1.42900 gm. respectively. The combining volume ratio at S.T.P. found by Burt and Edgar was H/O = 200.288 : 100. With these figures the weight of hydrogen combining with 8.000 parts of oxygen (*i.e.* the atomic weight of hydrogen) is :

$$\frac{2.00288 \times 0.089873 \times 8.000}{1.42900} = 1.00773.$$

Dissociation of water.—Water in the form of steam is decomposed at a high temperature into hydrogen and oxygen (p. 292): $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$, and to some extent into hydrogen and the hydroxyl radical: $\text{H}_2\text{O} \rightleftharpoons \text{H} + \text{OH}$. Liquid water is decomposed by exposure to ultra-violet light or α -rays from radium emanation; at first only hydrogen is evolved, the oxygen forming hydrogen peroxide: $2\text{H}_2\text{O} = \text{H}_2 + \text{H}_2\text{O}_2$, but afterwards oxygen is also evolved, probably from the hydrogen peroxide: $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$.

HYDROGEN PEROXIDE

History.—Hydrogen peroxide was discovered by Thenard in 1818; he obtained it by the action of dilute acids on barium peroxide and called it *oxygenated water*, since he showed that its formula corresponded to H_2O_2 .

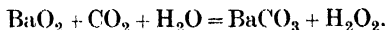
Occurrence.—Hydrogen peroxide vapour occurs in traces in the atmosphere and traces of hydrogen peroxide are said to be found in plants.

Preparation.—Hydrogen peroxide is *formed* in small quantities in the combustion of hydrogen: $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$. This may be demonstrated by allowing a hydrogen flame to play on a piece of ice and adding to the water formed a solution of titanium dioxide in sulphuric acid; a yellow colour develops, which is a sensitive test for hydrogen peroxide.

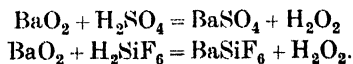
Hydrogen peroxide is formed by the combination of atomic hydrogen with the oxygen molecule, either by mixing gaseous atomic hydrogen (p. 170) with oxygen, or by bubbling oxygen under pressure past the cathode from which hydrogen is being evolved in electrolysis, when atomic hydrogen (*nascent hydrogen*) is first set free: $2\text{H} + \text{O}_2 = \text{H}_2\text{O}_2$.

Hydrogen peroxide is *prepared* by the action of an acid on a suitable metallic peroxide. To obtain a solution of hydrogen peroxide free from metallic salts, barium peroxide is used with an acid which forms an insoluble barium salt, such as carbonic, sulphuric or hydrofluosilicic acid. Potassium peroxide and tartaric acid may be used, when potassium hydrogen tartrate is precipitated.

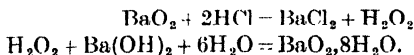
By passing carbon dioxide into a suspension of barium peroxide in distilled water, barium carbonate is precipitated and a solution of hydrogen peroxide is formed:



Anhydrous barium peroxide is not easily acted upon by dilute sulphuric acid since the particles become coated with insoluble barium sulphate. The hydrated barium peroxide $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ is easily decomposed by cold dilute sulphuric acid (1 vol. of acid to 5 vols. of water) or by hydrofluosilicic acid:

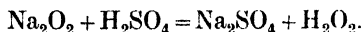


To prepare the hydrated barium peroxide, commercial barium peroxide is finely powdered and added a little at a time to a cold mixture of equal volumes of water and concentrated hydrochloric acid until the acid is neutralised. A little baryta solution is then added, which precipitates iron and aluminium impurities as hydroxides. These, with the silica contained in the barium peroxide, are filtered off, and the filtrate is added to saturated barium hydroxide solution. A white crystalline precipitate of hydrated barium peroxide is formed, which is filtered, washed with cold water free from carbon dioxide, and kept moist in a stoppered bottle :

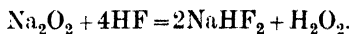


Barium peroxide also hydrates slowly when stirred with water and can then be decomposed by dilute sulphuric acid, or phosphoric acid. This method is used on the large scale. The barium sulphate precipitate is a valuable by-product used as a pigment (*blanc fixe*). The reaction of barium peroxide with sulphuric acid proceeds much more easily if a little hydrochloric acid is added.

Sodium peroxide added in small portions to 20 per cent sulphuric acid cooled in ice reacts as follows :



On cooling, much of the sodium sulphate separates as Glauber's salt $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, removing some water. The solution still contains some sodium sulphate, which does not interfere with some of its uses, but pure hydrogen peroxide solution may be obtained by distilling the solution in a vacuum (see below). Hydrofluoric acid may be used, when sodium hydrogen fluoride is precipitated :



Solutions of hydrogen peroxide are much more stable if a little sulphuric or phosphoric acid is present. Alcohol, glycerol, and barbituric acid are also stabilisers. Sodium stannate stabilises hydrogen peroxide in alkaline solution, in which it is otherwise unstable.

The strength of hydrogen peroxide solutions is stated in terms of the volume of oxygen evolved on heating, when the peroxide decomposes : $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. Commercial peroxide is usually 10 volumes or 20 volumes, according as it gives off 10 or 20 times its volume of oxygen. From the equation it is seen that 2×34 gm. of hydrogen peroxide evolve 32 gm. of oxygen, occupying 22.4 litres at S.T.P. Thus each gram of peroxide evolves 329.4 ml. of oxygen. A 1 per cent solution evolves 3.294 times its volume of oxygen ; 10 vol. peroxide is 3.04 per cent strength. A stronger solution on the market is "100 vol." or 30 per cent, with the trade name *perhydrol*, and a 90 per cent solution, which is fairly stable, is manufactured for special purposes.

A solution of hydrogen peroxide may be concentrated: (i) By freezing, when ice separates and the residual liquid is enriched in peroxide. (ii) By evaporation on a water bath, as hydrogen peroxide is appreciably less volatile than water; at a certain point, however, decomposition begins. (iii) By exposing the solution in a flat dish in an exhausted desiccator containing concentrated sulphuric acid: at a certain concentration the peroxide begins to volatilise, but by working at low temperatures Thenard obtained a liquid (density 1.452) evolving 475 vols. of O_2 at 14° , *i.e.* containing 95 per cent of H_2O_2 . (iv) By distillation under reduced pressure; this method was also used by Thenard. In 1894 Wolfenstein obtained practically pure hydrogen peroxide by the distillation of a concentrated solution under reduced pressure.

The apparatus used for distillation under reduced pressure (Fig. 116) consists of a distilling flask containing the solution of hydrogen peroxide

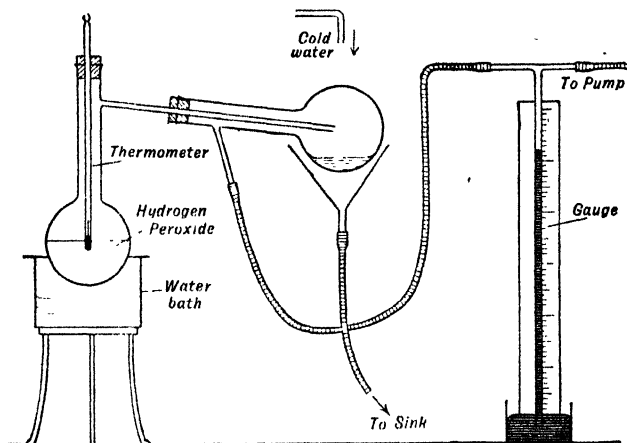
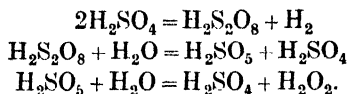


FIG. 116.—Distillation under reduced pressure.

placed on a water bath. The side tube is fitted by a rubber stopper to the inside of a second distilling flask, which serves as a receiver and is cooled by a stream of cold water. The side tube of this flask communicates by pressure tubing with a pressure gauge and a large empty bottle connected with a good water pump. A three-way stopcock allows air to be admitted to the apparatus when the receiver is changed. At first water comes over, since hydrogen peroxide has a higher boiling point. The later fraction is collected and redistilled under reduced pressure, when almost pure (99 per cent) hydrogen peroxide is obtained. A little of this is cooled in solid carbon dioxide and ether, and the solid obtained is added to the rest of the liquid cooled at -10° . Prismatic crystals of pure hydrogen peroxide, m.pt. -0.89° , separate.

Hydrogen peroxide is now manufactured in pure 30 per cent solution by the electrolysis of 50 per cent sulphuric acid, followed by vacuum distillation in a special apparatus. Persulphuric acid ($H_2S_2O_8$) is formed

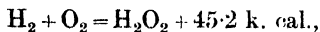
by electrolysis and on distillation this reacts with water to form first permonosulphuric acid (H_2SO_5) and then hydrogen peroxide :



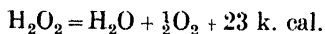
In another process, sulphuric acid containing ammonium sulphate is electrolysed and the resulting solution of ammonium persulphate is mixed with potassium sulphate to precipitate potassium persulphate $\text{K}_2\text{S}_2\text{O}_8$. This is distilled under low pressure with sulphuric acid to give a solution of hydrogen peroxide which may be concentrated by fractional distillation under low pressure up to 90 per cent H_2O_2 , which is fairly stable. This has been used to react with permanganates to give oxygen and steam for rocket propulsion, and also in burning fuels such as petrol, alcohol, and hydrazine hydrate in producing power.

Properties.—Pure hydrogen peroxide is a clear, syrupy liquid, density 1.465 at 0° , colourless in small amounts but with a bluish colour in bulk. It has an odour like that of nitric acid and a harsh metallic taste, and it blisters the skin. It freezes when cooled, m.pt. -0.89° . When rapidly heated to 151° , the b.pt. at atmospheric pressure, it explodes violently. Under reduced pressure the b.pt. is $84^\circ-85^\circ/68$ mm. and $69.2^\circ/26$ mm. The pure liquid has a strong *acid* reaction to litmus but in *pure* dilute solution hydrogen peroxide is quite neutral. The pure peroxide is fairly stable and can be kept for several weeks in the absence of sunlight, provided the glass of the bottle is perfectly smooth. In contact with rough surfaces or on shaking, decomposition occurs: $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$. Finely divided metals such as gold, silver and platinum (but not iron) cause explosive decomposition. Cotton wool and a mixture of magnesium or carbon powder with a trace of manganese dioxide, at once inflame. By mixing the pure peroxide with water and cooling in a mixture of solid carbon dioxide and ether, the crystalline hydrate $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ is obtained.

Hydrogen peroxide is formed *from its elements* with evolution of heat :



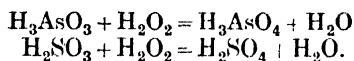
but decomposes into oxygen and water with evolution of heat :



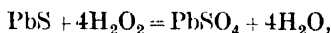
It is unstable at the ordinary temperature, tending to pass into water and oxygen.

† Hydrogen peroxide forms *addition compounds* with some salts, e.g. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$, and with urea, $\text{CON}_2\text{H}_4 \cdot \text{H}_2\text{O}_2$, and in these compounds it behaves like water of crystallisation. The crystalline compound with urea is called *hyperol*; it is stabilised by a little citric acid and forms hydrogen peroxide when dissolved in water.

Hydrogen peroxide is an active *oxidising agent*, one oxygen atom being easily removed, with formation of water. Arsenious and sulphurous acids are oxidised to arsenic and sulphuric acids :



Black lead sulphide is oxidised to white lead sulphate :

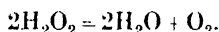


a reaction used in restoring discoloured oil paintings in which the white-lead pigment (basic lead carbonate) has been blackened by atmospheric hydrogen sulphide. Ferrous salts in acid solution are oxidised to ferric salts :

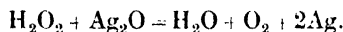


The oxidising action is used in bleaching delicate materials (wool, hair, silk, ivory, feathers) which would be injured by chlorine; the solution of the peroxide is made faintly alkaline with ammonia or added to 10 per cent sodium acetate solution. Hydrogen peroxide bleaches hair to a golden-yellow colour. It is also an antiseptic, and as it leaves no injurious products after its action it is largely used as a gargle, etc.

Platinum black and especially colloidal platinum (prepared by striking electric arcs between platinum wires under distilled water), bring about a rapid *catalytic decomposition* of hydrogen peroxide; the solution is also decomposed catalytically by manganese dioxide :

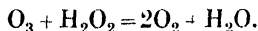


In some reactions hydrogen peroxide appears to act as a *reducing agent*. Thenard (1819) found that gold and silver oxides are reduced to the metals :

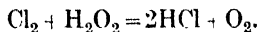


Brown silver oxide is precipitated by sodium hydroxide solution from silver nitrate solution and hydrogen peroxide solution added. There is a brisk effervescence of oxygen and the brown silver oxide is converted into black metallic silver. A further quantity of H_2O_2 added is *catalytically* decomposed by the finely divided silver.

Hydrogen peroxide slowly reduces ozone to oxygen :



Hydrogen peroxide is used as an *antichlor* to remove excess of chlorine from bleached fabrics :



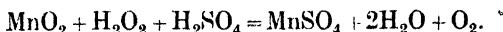
A solution of potassium permanganate acidified with sulphuric acid is readily reduced and decolorised by hydrogen peroxide, with evolution of oxygen :



This reaction is used in the titration of hydrogen peroxide solutions,

the permanganate being added from a burette until a pink colour appears.

Manganese dioxide liberates oxygen from a *neutral* solution of hydrogen peroxide, the action being catalytic, but in *acid* solution the manganese dioxide is reduced to a manganous salt and twice as much oxygen is evolved as from a neutral solution :

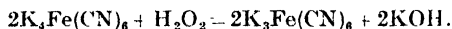


Solutions of bleaching powder and sodium hypobromite evolve oxygen :

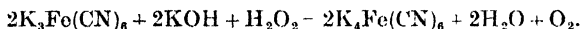


These reactions are also used in the determination of hydrogen peroxide, the gas evolved being measured in a gas burette.

An interesting case of the oxidising and reducing actions of hydrogen peroxide was discovered by Brodie. An *acid* solution of potassium ferrocyanide is *oxidised* by hydrogen peroxide to potassium ferricyanide :



An *alkaline* solution of potassium ferricyanide is *reduced* by hydrogen peroxide to potassium ferrocyanide with evolution of oxygen :



Tests for hydrogen peroxide.—Hydrogen peroxide may be detected by the liberation of iodine from potassium iodide, giving a blue colour with starch : $2\text{KI} + \text{H}_2\text{O}_2 = 2\text{KOH} + \text{I}_2$. The liberation of iodine occurs somewhat slowly but is rapid in presence of ferrous sulphate. Other substances, such as ozone and nitrites, liberate iodine from iodide.

A delicate test is the formation from chromium trioxide CrO_3 of a deep blue so-called "perchromic acid" CrO_5 . A *dilute* solution of potassium dichromate acidified with sulphuric acid is added to a dilute solution of hydrogen peroxide in a stoppered cylinder. The solution is rapidly shaken with ether, which floats to the surface with a beautiful blue colour : this solution slowly decomposes and a bluish-green solution of chromic sulphate is formed in the water layer.

The most delicate test for hydrogen peroxide is the formation of a yellow colour, due to titanium peroxide TiO_3 , with a solution of titanium dioxide in dilute sulphuric acid. This solution is prepared by heating TiO_2 with twice its volume of concentrated sulphuric acid, cooling, and diluting with water.

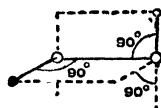
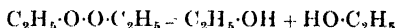
Other tests are : (1) guaiacol solution acidified with sulphuric acid gives a blue colour ; (2) guaiacum tincture, with a little blood or malt extract, gives a blue colour (this is also a delicate test for blood, and can be used in identifying blood-stains) ; (3) a mixture of aniline and potassium chlorate, dissolved in dilute sulphuric acid, gives a violet colour ; (4) filter-paper soaked in a solution of cobalt naphthenate and dried, changes from rose to olive-green with hydrogen peroxide.

Formula of hydrogen peroxide.—The vapour density of hydrogen peroxide as determined under reduced pressure at 90° is 17 (H = 1) ; the molecular weight found from the freezing point of the aqueous solution (p. 247) is 34 ; hence the formula is H₂O₂.

The constitutional formula may be H·O·O·H, *i.e.* dihydroxyl HO·OH. This agrees with the instability of compounds which contain chains of directly linked oxygen atoms.

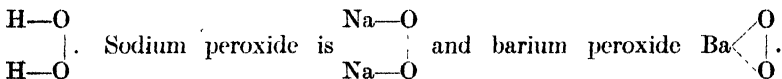
In order to account for the instability of one oxygen atom, which suggests that it is linked differently from the other, Buff (1866) and Kingzett (1882) wrote the formula as O = O = H₂, in which one oxygen is quadrivalent. In the modern theory of valency the maximum covalency of oxygen is three, and this formula should be written as [O = O - H] - H⁺, a weak acid.

By the action of hydrogen peroxide on diethyl sulphate (C₂H₅)₂SO₄, Baeyer and Villiger (1900) obtained diethyl peroxide (C₂H₅)₂O₂, and by the action of zinc and acetic acid this is reduced to ethyl alcohol C₂H₅·OH. This agrees with the formula C₂H₅·O·O·C₂H₅ :



This suggests that the formula of hydrogen peroxide is H·O·O·H. The X-ray spectrum of pure liquid H₂O₂ shows that the two hydrogen atoms are fixed in two perpendicular planes passing through the O—O axis, as shown in the figure.

H₂O₂ is a *true peroxide* containing two singly linked oxygen atoms :



True peroxides give hydrogen peroxide with dilute acids and differ in constitution from *dioxides* of lead, manganese, etc., which contain higher valency states of the metals and give oxygen with concentrated sulphuric acid and chlorine with concentrated hydrochloric acid. Their formulae are of the type O=Pb·O. This is confirmed by the formation of unstable higher chlorides with cold concentrated hydrochloric acid, *e.g.* PbCl₄. With concentrated hydrochloric acid, however, barium peroxide evolves chlorine (Brodie, 1863) :

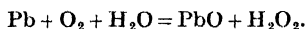


Autoxidation.—The formation of hydrogen peroxide during the slow oxidation of phosphorus, oil of turpentine, and metals by gaseous oxygen in the presence of water was studied by Schönbein in 1858. He found that the oxygen is equally divided in oxidising the substance (*e.g.* lead) and in forming hydrogen peroxide. Such a reaction is called *autoxidation*.

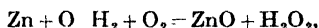
He supposed that *atomic oxygen* exists in two forms, negative ozone ⊖ and positive antiozone ⊕. The antiozone formed hydrogen peroxide with

water or oxidised indigo or other oxidisable substance. Brodie (1850) showed that all the supposed reactions of antozone are due to hydrogen peroxide.

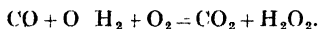
Brodie, and Clausius (1858), considered that the oxygen molecule, which they thought contained two atoms of opposite polarities, is divided in autoxidation reactions, one atom oxidising a substance and the other forming with water a molecule of hydrogen peroxide :



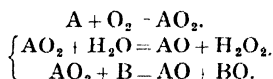
Traube (1882) suggested that the oxygen molecule unites as a whole with the oxidisable substance to form a *holoxide* or *moloride*. For example, in the combustion of hydrogen, H_2 unites with O_2 to form hydrogen peroxide as a primary product : $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$. The reaction between zinc, water and oxygen he represented as :



and the primary oxidation of carbon monoxide as :



Bach (1897) concluded that the substance undergoing oxidation (*autoxidiser* A) itself unites with a molecule of oxygen to form an unstable higher oxide, which may then react with water or some other *acceptor* B to give the lower oxide of A and H_2O_2 or BO :

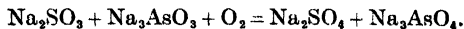


With metals, the unstable higher oxides PbO_2 , ZnO_2 , are not the ordinary known ones, which do not give hydrogen peroxide with water.

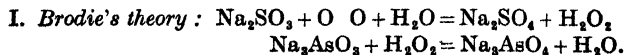
According to Engler and Wild, the oxygen molecule is first opened up to form $-\text{O}-\text{O}-$, which combines with the *activator* (e.g. turpentine) to form the unstable peroxide. In some cases these unstable peroxides have been isolated. The bleaching and disinfecting properties of turpentine are due to its ability to activate oxygen in this way, and it forms a peroxide on standing in a loosely stoppered bottle.

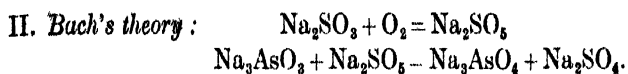
If a little turpentine is added to dilute potassium iodide and starch solution in an open flask, and the mixture shaken and allowed to stand, a blue colour is produced.

Induced oxidation.—A solution of sodium arsenite Na_3AsO_3 is not oxidised to arsenate on exposure to air, but a solution of sodium sulphite Na_2SO_3 is oxidised to sulphate. When a solution containing both arsenite and sulphite is exposed to air, *both* salts are oxidised :



This induced oxidation may be explained on Brodie's or on Bach's theories. The Na_2SO_3 is called an *inductor*, the O_2 molecule the *actor*, and the Na_3AsO_3 (which is not oxidised by itself) the *acceptor* :





Deuterium peroxide.—A “heavy” hydrogen peroxide, *deuterium peroxide* D_2O_2 , is formed by passing “heavy steam” (D_2O vapour) through a mixture of deuteriosulphuric acid D_2SO_4 and potassium persulphate $\text{K}_2\text{S}_2\text{O}_8$ (which form D_2SO_5 , undergoing hydrolysis by D_2O) and condensing the vapour. The solution of D_2O_2 in D_2O thus obtained is fractionated, and pure D_2O_2 obtained (Fehér, 1939). HDO_2 is also known.

CHAPTER XIV

CHLORINE

History.—In 1658 Glauber obtained “spirit of salt” by distilling common salt with concentrated sulphuric acid and dissolving the evolved gas in water. The other product of the reaction was sodium sulphate, called Glauber’s salt. In 1772 Priestley found that the gas, which is very soluble in water, could be collected over mercury. The solution is spirit of salt, then called *muriatic acid*. Lavoisier (1789) regarded it, like other acids, as the oxide of a non-metallic element then unknown and called by him the *muriatic radical*.

In 1774 Scheele had examined the action of concentrated muriatic acid on “black manganese” (manganese dioxide). This dissolved in the cold acid to form a dark-brown solution, which on warming gave off a greenish-yellow gas which had a powerful odour and bleached vegetable colours. Scheele said this gas was muriatic acid deprived of phlogiston by the manganese, and since he thought hydrogen was phlogiston, this means muriatic acid deprived of hydrogen, which is correct.

In 1785 Berthollet exposed a solution of the greenish-yellow gas in water to light, when it gave off bubbles of oxygen and left a solution of muriatic acid. Hence he considered that the gas was a compound of muriatic acid and oxygen, or *oxymuriatic acid*.

The production of oxymuriatic acid by the action of oxidising agents (*e.g.* manganese dioxide) on muriatic acid, and Berthollet’s experiment, both seemed to show that oxymuriatic acid was a higher oxide of the muriatic radical. All that remained was to isolate the muriatic radical and this was regarded as a task for the future.

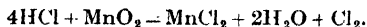
In 1810 Davy tried to decompose oxymuriatic acid into oxygen and the muriatic radical. He burnt phosphorus in the gas, expecting to get phosphorus pentoxide, but the products were a volatile liquid (phosphorus trichloride) and a solid (phosphorus pentachloride) quite different from phosphorus pentoxide. On heating sulphur in the gas he did not obtain sulphur dioxide but a liquid (chloride of sulphur). Charcoal even when heated in the gas at a very high temperature (the electric arc) did not form any carbon dioxide but was entirely without action.

Since all the products obtained from “oxymuriatic acid” weighed more than the gas, and since no compounds known to contain oxygen could be formed from it, Davy concluded that “oxymuriatic acid” is really an element and called it *chlorine*, derived from the Greek *chloros* = pale green. Muriatic acid is a compound of hydrogen and chlorine, and should be called hydrochloric acid. Davy showed that in Berthollet’s experiment the oxygen came from the water, the hydrogen of which united with the chlorine to form hydrochloric acid :



He found that *dry* chlorine does not bleach and the bleaching action is due to nascent oxygen liberated from the water which must be present.

The production of chlorine from muriatic acid and higher oxides (*e.g.* manganese dioxide) is explained by the oxidation of the hydrogen of the acid, setting free the chlorine :

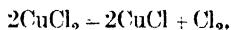


This may be shown by passing dry hydrogen chloride gas over some dry manganese dioxide heated in a bulb tube, when chlorine is evolved and moisture condenses on the cool part of the tube.

Preparation.—Chlorine is evolved on heating gold, platinum and cupric chlorides ; the lower chlorides of platinum and gold are first formed but decompose at higher temperatures :

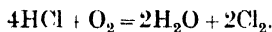


cupric chloride decomposes into chlorine and the stable cuprous chloride :

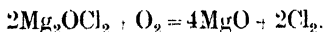


Pure chlorine can be prepared by the electrolysis of fused silver chloride with carbon electrodes : $2\text{AgCl} = 2\text{Ag} + \text{Cl}_2$.

Hydrogen chloride gas is oxidised by free oxygen when a mixture of hydrogen chloride gas with oxygen or air is passed over a heated copper salt acting as a catalyst :



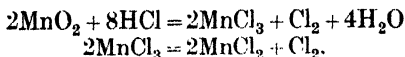
Chlorine (mixed with nitrogen) is formed by passing air over strongly heated magnesium oxychloride :



The common *laboratory method* for the preparation of chlorine is to heat 100 gm. of manganese dioxide (best in small lumps) with 300 ml. of concentrated hydrochloric acid in a flask (Fig. 117) :



The reaction probably takes place in two stages ; a higher chloride of manganese MnCl_3 is first formed in the cold as a dark-brown solution, which decomposes on heating into chlorine and manganous chloride MnCl_2 :



The gas is washed with a little water to free it from hydrochloric acid and is collected in dry jars by downward displacement, since it is $2\frac{1}{2}$ times as heavy as air, is fairly soluble in water, and attacks mercury.

Chlorine has a powerful action on the mucous membranes and the experiment is best performed in a fume cupboard. The gas may also be collected

over a saturated solution of common salt. It may be dried by calcium chloride, concentrated sulphuric acid, or phosphorus pentoxide.

Instead of using hydrochloric acid, a mixture of common salt, manganese dioxide and 50 per cent sulphuric acid may be heated, when hydrochloric acid is first produced and is then oxidised by the manganese dioxide ; this mixture evolves a *slow* stream of chlorine in the cold :

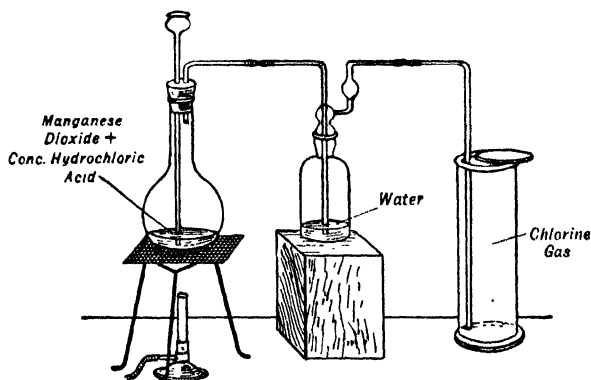
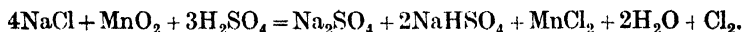
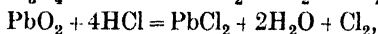
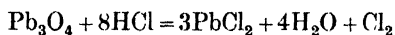
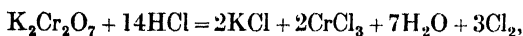


FIG. 117—Preparation of chlorine.

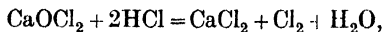
Chlorine is evolved on heating concentrated hydrochloric acid with red lead or lead dioxide :



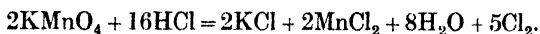
or concentrated hydrochloric acid with potassium dichromate :



and by dropping cold concentrated hydrochloric acid on bleaching powder :



or on potassium permanganate :



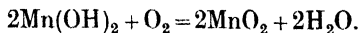
Pure chlorine may be obtained by drying with concentrated sulphuric acid the chlorine obtained from hydrochloric acid and potassium permanganate, liquefying it in a bulb immersed in a mixture of solid carbon dioxide and ether, and then evaporating the liquid chlorine. Pure chlorine is completely absorbed by mercury, even if the materials are very dry (see p. 206).

The Weldon process.—Chlorine was formerly made on the technical scale from manganese dioxide and the hydrochloric acid obtained in the Leblanc process (p. 210) by heating with steam in stone tanks. To

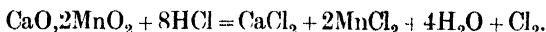
recover the manganese from the residual liquor, *Weldon's process* was used. An *excess* of milk of lime was added to precipitate manganous hydroxide :



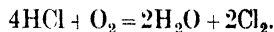
The liquid was heated by steam and air blown through. *In presence of excess of lime* the manganous hydroxide oxidises to manganese dioxide :



This is a weakly acidic oxide and combines with lime to form a precipitate of calcium manganite CaO, MnO_2 . Some more manganese liquor was added and the air blowing continued, when the CaO, MnO_2 was converted into CaO, 2MnO_2 , called *Weldon mud*. This was decomposed by hydrochloric acid to give chlorine, and the process repeated :



The Deacon process.—Hydrogen chloride gas is oxidised by *free* oxygen when a mixture of oxygen or air and hydrogen chloride is passed over a heated catalyst containing cupric chloride :



A stream of air is passed through concentrated sulphuric acid in a Woulfe's bottle, into which concentrated hydrochloric acid is allowed to drop slowly. The mixture of air and hydrogen chloride gas is passed through

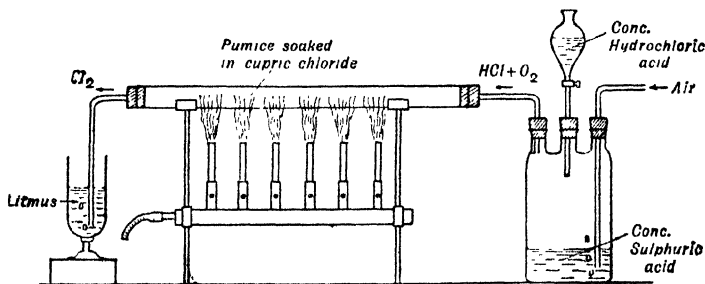
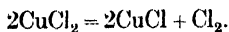


FIG. 118.—Principle of the Deacon process.

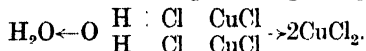
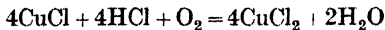
a hard glass tube packed with pieces of pipe-clay or pumice which have been soaked in a solution of cupric chloride and dried, and the tube is heated (Fig. 118). The gas may be passed through litmus solution, which is bleached.

This reaction is used on the large scale as the *Deacon process*. It is not suitable for the laboratory preparation, since the chlorine obtained is diluted with atmospheric nitrogen.

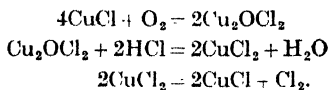
The catalytic action of the copper salt has been explained as follows. The cupric chloride decomposes on heating to form cuprous chloride and chlorine :



In presence of oxygen and cuprous chloride the hydrogen chloride is decomposed to form water and cupric chloride, and the reaction then begins again :



It is sometimes assumed that an oxychloride of copper is formed :



Copper sulphate used as a catalyst is first converted into cupric chloride :



Since the reaction $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$ is reversible there is always some hydrogen chloride mixed with the chlorine, and in the Deacon process this is removed by washing with water. The gas is then dried with sulphuric acid: it contains only 5 to 7 per cent of chlorine and is used to make bleaching powder.

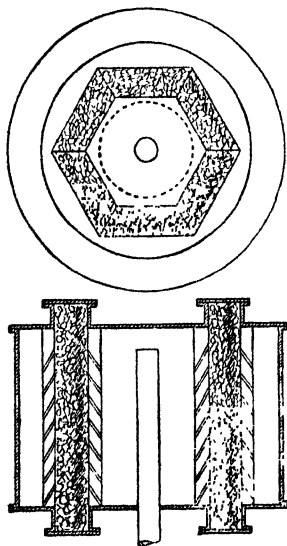
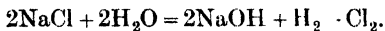


FIG. 119.—Deacon converter.

at the anode and sodium hydroxide and hydrogen are formed at the cathode (see page 242) :



Various types of electrolytic cell are used, the main object being to prevent the chlorine evolved at the anode from coming in contact with the alkali formed at the cathode, when reaction would occur between them.

On the large scale hydrogen chloride from salt cake furnaces (p. 210) is purified by dissolving in water, mixing with concentrated sulphuric acid, and blowing out the pure gas with a current of air. The mixture of air and hydrogen chloride then passes over pieces of broken bricks impregnated with a little cupric chloride and heated at 450° in a converter (Fig. 119) divided into compartments, so that part of the mass can be removed and replaced when it loses its catalytic activity.

Electrolytic processes.—Nearly all the chlorine used technically is now obtained by the electrolysis (see p. 218) of a solution of common salt. Chlorine is deposited

The **Castner-Kellner cell** consists (Fig. 120) of a shallow slate tank divided into three compartments by slate partitions not quite touching the floor, which is covered by a pool of mercury separating the three compartments. Each end compartment contains strong brine and the middle one water. Anodes of carbon are in the end compartments, and the cathode, a bundle of iron rods, is in the central compartment. Most of the current passes from the mercury in the central compartment to the iron cathode and the rest through a resistance in parallel. Chlorine evolved in the end compartments is led off by earthenware pipes. Sodium discharged

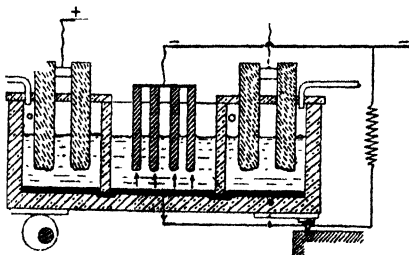


FIG. 120.—The Castner-Kellner cell.

on the mercury in the end compartments, acting as a cathode, dissolves to form sodium amalgam. The cell is given a slow rocking motion by an eccentric and the amalgam is brought from the end compartments to the middle compartment, where it acts as an anode and the sodium decomposes the water, forming a solution of sodium hydroxide. Hydrogen is evolved from the iron cathode. In the modern process, the cell is not rocked but the mercury is passed through the cell and the amalgam decomposed by water in a separate vessel.

In the **Gibbs cell** (Fig. 121) the anodes are carbon rods separated by a diaphragm of asbestos paper from the cylindrical perforated iron cathode,

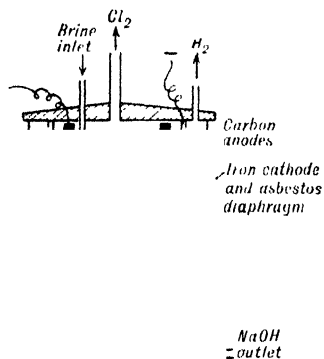


FIG. 121.—Gibbs cell.

on the outside of which the sodium hydroxide solution forms. The solution of sodium hydroxide is not so pure as that obtained in the Castner-Kellner cell, and the sodium chloride contained in it must be separated by evaporating, when the sodium chloride deposits from the concentrated sodium hydroxide solution.

Most of the chlorine is used for bleaching and in refining petroleum, either as such or (usually) as *hypochlorites* of sodium or calcium, the latter in the form of *bleaching powder*. Some is used to make synthetic hydro-

chloric acid, in making solvents (chlorinated acetylene), for chlorinating water supplies, liberating bromine from sea water, and making some chemicals such as carbonyl chloride and sulphur chloride.

Electrolytic chlorine is fairly easily liquefied by cooling and compression. The liquid is transported in cylinders or tank wagons of steel, since this metal is not attacked by *dry* chlorine.

Properties of chlorine.—Chlorine is a greenish-yellow gas with an irritating odour and a violently corrosive action on the mucous membranes. The density of chlorine gas (3.214 gm. per litre at S.T.P.) is a little higher than would be expected from the formula Cl_2 , which may indicate slight association into Cl_4 .

The relative density falls slightly with rise of temperature, becoming normal at about 240° , and remaining normal up to 1200° . The density at 1150° was found by Renganum (1905) by comparing the volumes of gas displaced from a small quartz Victor Meyer apparatus, in one case filled with oxygen and in the other with chlorine. They were equal, hence no dissociation occurred. Crafts (1880) obtained the same result by displacing oxygen by chlorine, or chlorine by oxygen, in a porcelain apparatus at 1350° . According to Victor Meyer and Langer (1885), the density of chlorine at 1400° fell to 29.29 ($H = 1$), corresponding with 21 per cent dissociation into atoms: $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$. Pier (1908), from specific heat measurements, assumed a dissociation of Cl_2 above 1450° , but the value given by Victor Meyer and Langer appears to be too high. At very low pressures the dissociation is appreciable at 700° – 900° (Henglein, 1922).

Chlorine when passed into a tube cooled in solid carbon dioxide and ether condenses to an amber-yellow liquid, boiling at -34.5° . On cooling in liquid air this forms a pale-yellow solid, melting at -100.9° . The critical temperature of chlorine is 140.9° , the critical pressure 76.1 atm.

Chlorine is a very active element: it readily combines directly with hydrogen and most metals and non-metallic elements except nitrogen, oxygen, and carbon. Reaction often occurs at the ordinary temperature, frequently with flame or incandescence.

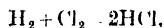
The reaction with metals does not always take place if the materials are dry, although pure dry mercury completely absorbs pure dry chlorine. Andrews (1842) found that dry copper and zinc do not react with dry chlorine. Reaction with dry materials occurs with arsenic, antimony, mercury and phosphorus. Bromine behaves similarly. Sodium may be melted in dry chlorine without reaction taking place (Wanklyn, 1883). In the following experiments, undried chlorine should be used.

Sprinkle a little finely powdered arsenic and antimony into jars of chlorine. The substances burn, producing poisonous fumes of the chlorides AsCl_3 and SbCl_5 .

A piece of phosphorus in a deflagrating spoon ignites spontaneously in chlorine, burning with a pale flame and producing fumes of PCl_5 .

Pass chlorine over a piece of sodium strongly heated in a hard glass bulb tube (Fig. 122). The metal burns with a very brilliant yellow flame, producing NaCl .

A jet of hydrogen burning in air continues to burn with an enlarged greenish flame in a jar of chlorine (Fig. 123), producing hydrogen chloride:



A jet of chlorine burns with a grey needle-shaped flame when introduced into an inverted jar of hydrogen which is burning at the mouth.

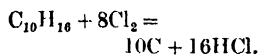
A piece of dry red flannel and some dry litmus paper suspended in a jar of chlorine containing some concentrated sulphuric acid to dry the gas, are not bleached. In moist chlorine bleaching occurs.

A burning taper burns in a jar of chlorine with a small dull-red flame, clouds of black carbon and white fumes of hydrochloric acid being evolved. Paraffin wax is a mixture of hydrocarbons, the chlorine removes the hydrogen forming HCl, and sets free the carbon, with which it does not combine directly.

A mixture of 2 vols. of chlorine and 1 vol. of methane CH_4 in a gas jar, burns when kindled with a taper, giving fumes of hydrochloric acid and a cloud of carbon : $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$.

A mixture of 2 vols. of chlorine and 1 vol. of ethylene C_2H_4 when kindled with a taper, burns with a red flame, emitting a dense black cloud of carbon and fumes of hydrochloric acid : $\text{C}_2\text{H}_4 + 2\text{Cl}_2 = 2\text{C} + 4\text{HCl}$.

A little turpentine $\text{C}_{10}\text{H}_{16}$ poured on filter-paper catches fire when plunged into a jar of chlorine, giving a black cloud of carbon and fumes of hydrochloric acid :



Chlorine combines directly with sulphur dioxide SO_2 , carbon monoxide CO , and ethylene C_2H_4 , forming sulphuryl chloride SO_2Cl_2 , carbonyl chloride (phosgene) COCl_2 , and ethy-

lene dichloride $\text{C}_2\text{H}_4\text{Cl}_2$, respectively. The carbon monoxide and sulphur dioxide react with chlorine in presence of animal charcoal ; ethylene combines with chlorine on exposure to light.

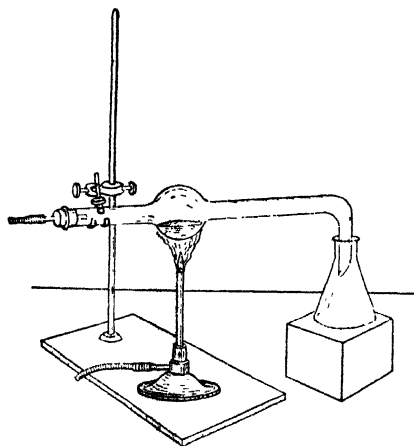


FIG. 122.—Combustion of sodium in chlorine.

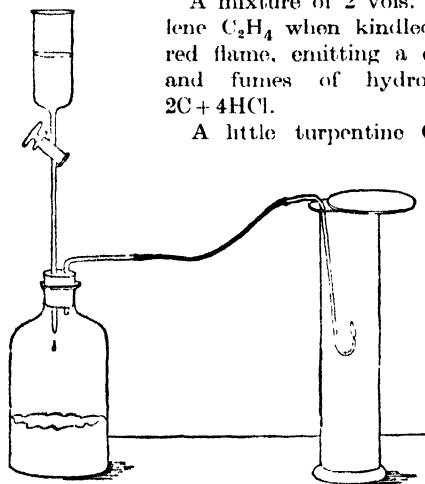
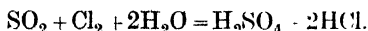


FIG. 123.—Combustion of hydrogen in chlorine.

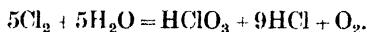
Chlorine water.—Chlorine is fairly soluble in water, 2.68 volumes of gas dissolving in 1 volume of water at 15°. The volumes of chlorine reduced to 0° C. and a total pressure (gas + water vapour) of 760 mm. dissolved by 1 volume of water are :

0°	10°	15°	20°	25°	30°	40°	50°	60°
4.61	3.095	2.635	2.260	1.985	1.769	1.41	1.20	1.0

Below 9.6° the saturated solutions are metastable, being supersaturated with respect to the solid chlorine hydrate, in presence of which the solubility has a maximum value, 2.98, at 9.6°. The solution prepared by passing chlorine into water is yellow, smells strongly of the gas, and is called *chlorine water*. It has bleaching and oxidising properties, precipitates sulphur from a solution of hydrogen sulphide ; $\text{H}_2\text{S} + \text{Cl}_2 = 2\text{HCl} + \text{S}$, and liberates iodine from potassium iodide solution : $2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2$; with an excess of chlorine water the iodine reacts to form iodine chloride ICl . A solution of sulphur dioxide (sulphurous acid) is oxidised to sulphuric acid :



When chlorine water in a flask inverted in a basin of the same liquid is exposed to *bright sunlight*, it is decomposed with evolution of oxygen, and a solution of hydrochloric acid remains : $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$. In diffused daylight some chloric acid is formed :



Chlorine is more soluble in concentrated hydrochloric acid than in water, perhaps because a compound HCl_3 is formed.

Chlorine hydrate.—If chlorine is passed into water cooled in ice, almost white crystals separate. This substance, discovered by Berthollet in 1785, is chlorine hydrate. Its composition has been stated to be $\text{Cl}_2, 10\text{H}_2\text{O}$ (Faraday, 1823), $\text{Cl}_2, 8\text{H}_2\text{O}$ (Roozeboom, 1884), $\text{Cl}_2, 7\text{H}_2\text{O}$ (de Forcrand, 1902), and (according to Bouzat and Azinières, 1923) $\text{Cl}_2, 6\text{H}_2\text{O}$ if prepared in presence of liquid chlorine. The crystals are stable in a sealed tube at room temperature. When gently warmed the crystals melt with effervescence and chlorine is evolved ; if the experiment is carried out in the dark, the gas after drying is very pure (Harker, 1892).

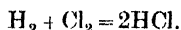
If crystals of chlorine hydrate sealed up in a strong tube are warmed, they melt and liquid chlorine is formed.

HYDROGEN CHLORIDE (HYDROCHLORIC ACID)

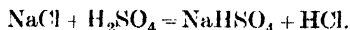
Occurrence.—Hydrogen chloride is found in some volcanic gases and in solution in some rivers in volcanic districts. Small quantities of free hydrochloric acid occur in human (0.2 to 0.4 per cent) and animal (3 per cent in dog's) gastric juice.

Preparation.—Hydrogen chloride is formed by the combustion of hydrogen in chlorine or chlorine in hydrogen, and by the explosion of

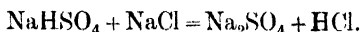
a mixture of the two gases when kindled, sparked, or exposed to light :



It is usually made by heating a mixture of concentrated sulphuric acid and common salt :



Sodium hydrogen sulphate (or sodium bisulphate) NaHSO_4 is formed unless the temperature is higher than can be reached in a glass flask, but when *strongly* heated with common salt it forms hydrochloric acid and normal sodium sulphate :



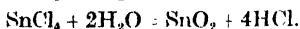
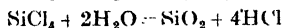
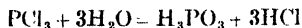
In the *laboratory preparation* common salt (sometimes rock salt or salt which has been fused) is placed in a fairly large flask (to allow space for frothing) and concentrated sulphuric acid added through a thistle funnel. Some gas is evolved at once but when the reaction slackens the flask is gently heated on wire gauze. The gas is collected in dry jars by downward displacement, as it is rather heavier than air. When the jar is filled with gas copious white fumes issue from the mouth. These are formed by atmospheric moisture producing a mist of small droplets of concentrated hydrochloric acid ; the dry gas is quite transparent and it does not fume with *dry* air. The gas may be dried by concentrated sulphuric acid or calcium chloride and collected over mercury.

The gas should not be dried by phosphorus pentoxide, as this slowly absorbs it, 227 ml. of dry gas being taken up by 1 gm. of pentoxide : $2\text{P}_2\text{O}_5 + 3\text{HCl} = \text{POCl}_3 + 3\text{HPO}_3$.

A convenient method of obtaining the gas is to use a Kipp's apparatus charged with concentrated sulphuric acid and lumps of sal ammoniac, when a regular stream of gas is evolved : $\text{NH}_4\text{Cl} + \text{H}_2\text{SO}_4 = \text{NH}_4\text{HSO}_4 + \text{HCl}$.

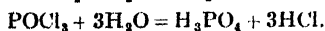
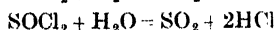
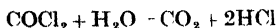
Many other metal chlorides (*e.g.* of potassium, calcium, aluminium, iron, etc.) evolve hydrogen chloride with concentrated sulphuric acid ; lead, cuprous, silver and mercurous chlorides react slowly, and mercuric chloride not at all.

Hydrogen chloride is also evolved by the action of water on the chlorides of many non-metals : arsenic, boron, phosphorus, silicon and sulphur (but not carbon), and on stannic chloride :



Of these, only boron chloride BCl_3 , titanium chloride TiCl_4 , and stannic chloride react in the gaseous state with water vapour.

Carbon, sulphur and phosphorus oxychlorides are also decomposed by water :



Very pure hydrogen chloride gas is prepared by the action of water on silicon chloride, since that from sodium chloride and sulphuric acid contains a trace of hydrogen sulphide.

On the technical scale hydrogen chloride and sodium sulphate are made by heating common salt and concentrated sulphuric acid in a *salt-cake furnace* (Fig. 124) containing an iron pan *A* for the first stage of the process with formation of NaHSO_4 , and a hearth or fire-clay box (*muffle*)

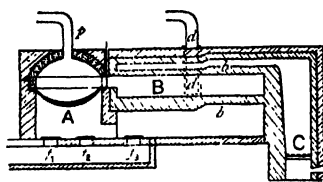
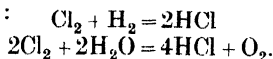


FIG. 124.—Salt-cake muffle furnace.

B, into which the pasty mass from the pan is raked and is strongly heated by the flames from the producer *C* to form Na_2SO_4 (*salt cake*). The gas is absorbed by water trickling over coke or pottery cylinders in a large brickwork or stone tower to form a solution of hydrochloric acid called *spirit of salt* or *muratic acid*, which may be yellow on

account of impurities (*e.g.* iron salts). This acid is transported in large globular glass bottles called *carboys* packed with straw into iron crates, or in large stoppered bottles called *Winchester quarts*. The acid is used for cleaning metals (*e.g.* iron sheets before galvanising) and other purposes.

Synthetic hydrochloric acid is made by burning electrolytic chlorine in electrolytic hydrogen in silica tubes, and dissolving in distilled water; in another process chlorine and steam are passed over heated active charcoal as a catalyst:



Properties.—Hydrogen chloride is a colourless gas, normal density 1.6392 gm. per litre, with a very pungent irritating odour, and it attacks the mucous membranes of the nose and throat. It is not combustible and is a non-supporter of combustion. It is liquefied with difficulty. The liquid is colourless, b.pt. -85.0° , density at the b.pt. 1.184, critical temperature 51.45° , critical pressure 81.55 atm. When the gas is passed into a tube cooled in liquid air a white solid, m.pt. -111.4° , is formed.

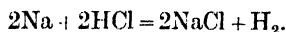
The very dry liquid is without action on zinc, iron, magnesium, quicklime, and some carbonates, all of which are readily dissolved by the aqueous acid, but it readily dissolves aluminium with evolution of hydrogen: $2\text{Al} + 6\text{HCl} = 2\text{AlCl}_3 + 3\text{H}_2$. The liquid expands on heating between -80° and $+30^\circ$ more rapidly than a gas.

When very strongly heated, hydrogen chloride gas is slightly dissociated: $2\text{HCl} \rightleftharpoons \text{H}_2 + \text{Cl}_2$; percentage dissociation:

$t^\circ\text{C.}$	427	727	1537	1727
% -	1.1×10^{-5}	1.34×10^{-3}	0.274	0.41

The gas is also decomposed to some extent by radium emanation and by ultraviolet light.

Burning sodium introduced into a jar of the gas burns with a bright yellow flame, producing solid sodium chloride and liberating hydrogen :



Aqueous hydrochloric acid.—Hydrogen chloride is very soluble in water. When 1 kgm. of water is saturated with the gas at 15° it increases in weight to 1.75 kgm., and the density is 1.231. It contains about 43 per cent of HCl ; the commercial acid contains about 39 per cent and its density is 1.20. The concentrated acid fumes strongly in air.

DENSITIES OF SOLUTIONS OF HYDROCHLORIC ACID AT 15°.

p.c. HCl	Density D_{15}^{15}	p.c. HCl	Density D_{15}^{15}
2.14	1.010	24.78	1.125
10.17	1.050	29.57	1.150
15.16	1.075	34.42	1.175
20.01	1.100	39.11	1.200

The great solubility of hydrochloric acid gas in water may be shown by the *fountain experiment*. A large round-bottomed flask is filled with the gas by displacement (this takes some time) and fitted with a rubber stopper carrying a tube drawn out to a jet. The flask is inverted with the tube dipping into water coloured with blue litmus solution as shown in Fig. 125. By blowing into the short tube on the second flask a little water is forced into the upper flask. The gas dissolves, the atmospheric pressure forces the water in the lower flask as a fountain into the upper flask, and the litmus is turned red by the acid solution formed.

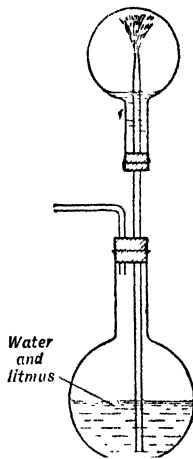


FIG. 125.— Demonstration of the solubility of hydrogen chloride.

When hydrochloric acid containing 20.24 per cent of HCl is distilled under 760 mm. pressure, the acid passes over completely at 110° without change of composition, as though it were a pure substance. If a weaker acid (*e.g.* 15 per cent) is taken, a more dilute acid passes over until the residue contains 20.24 per cent of HCl ; if a stronger acid (*e.g.* 30 per cent) is distilled it loses hydrogen chloride until the 20.24 per cent acid is left. In both cases the residual acid distils without change of composition. Since the composition remains constant during distillation, the vapour has the same composition as the liquid, hence the boiling point (110°) remains constant. This is the *maximum boiling point* for the aqueous acid ; weaker and stronger solutions boil at lower temperatures.

Roscoe and Dittmar (1860) found that the concentration of the acid of maximum boiling point decreases with rise of pressure in distillation :

Pressure mm. Hg - - - -	50	700	760	800	1800
Per cent HCl in max. b. pt. acid -	23.2	20.4	20.24	20.2	18.7

By passing hydrogen chloride gas into the concentrated acid at -23° Pierre and Pouchot obtained a crystalline hydrate $\text{HCl}\cdot 2\text{H}_2\text{O}$ (m. pt. -18°), decomposing on warming. Rupert (1907) obtained another crystalline hydrate $\text{HCl}\cdot \text{H}_2\text{O}$.

Formula of hydrogen chloride.—The composition of hydrogen chloride may be determined either by *analysis* or by *synthesis*.

Analytical methods.—(i) Hydrochloric acid (sp. gr. 1.1) is electrolysed with gas-carbon electrodes (Fig. 126), since platinum is attacked by chlorine. When the acid is saturated with chlorine, equal volumes of hydrogen and chlorine are evolved.

(ii) The closed limb of the U-tube shown in Fig. 127 is filled with dry hydrogen chloride gas.

The lower stopcock is closed and the open limb nearly filled with liquid sodium amalgam. This stopcock is then opened so as to bring the gas in contact with the amalgam, and the apparatus is allowed to stand. A white crust of sodium chloride is

FIG. 126. — Electrolysis of hydrochloric acid.

slowly formed, and the volume of gas after levelling is decreased to half. When mercury is poured into the open limb of the U-tube to displace the gas through the upper stopcock, it will be found to be inflammable, and is hydrogen.

This experiment shows that 1 vol. of hydrogen chloride contains $\frac{1}{2}$ vol. of hydrogen, or (by Avogadro's hypothesis) 1 molecule of hydrogen chloride contains $\frac{1}{2}$ molecule or 1 atom of hydrogen, and hence the formula is HCl_x . The density of the gas gives the molecular weight 36.5. This contains 1 part of hydrogen, hence it contains 35.5 parts, or 1 atom, of chlorine and the formula is HCl .

Synthetic method.—The composition of hydrogen chloride may be shown by synthesis from hydrogen and chlorine.

(i) One half of a tube provided with stopcocks (Fig. 128) is filled with chlorine and the other half with hydrogen. The middle stopcock is opened and the gases allowed to mix in a room with diffused daylight (in *sunlight* the gases combine with explosion). After a few hours combination is

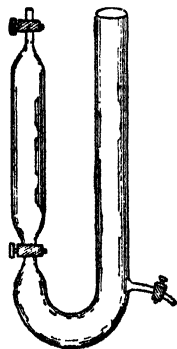
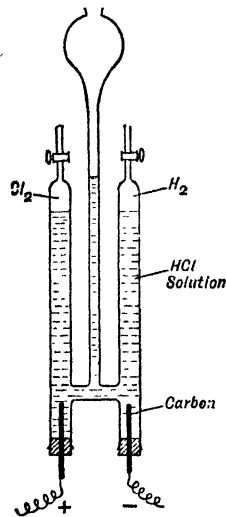


FIG. 127. — Decomposition of hydrogen chloride by sodium amalgam.

complete and the greenish colour of the chlorine disappears. One of the end stopcocks is opened under mercury and it is seen that there is no change in volume; if it is opened under water this dissolves the hydrogen chloride and fills the tube (provided the hydrogen and chlorine were pure and exactly equal volumes were used).

(ii) A dry mixture of equal volumes of hydrogen and chlorine is passed in the dark into the tube shown in Fig. 129 provided with platinum wires for exploding the gas by a spark. *The tube is placed behind a strong glass screen*



FIG. 128.—Synthesis of hydrogen chloride.

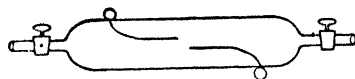


FIG. 129.—Explosion of a mixture of hydrogen and chlorine.

(in case it should burst) * and a spark is passed. There is a flash of light in the tube and a sharp click is heard. When the tube has cooled it is opened under mercury and water successively, with similar results to those described above.

These experiments show that :

1 vol. hydrogen + 1 vol. chlorine = 2 vols. hydrogen chloride.

Thus 2 molecules of hydrogen chloride contain 1 molecule of hydrogen and 1 molecule of chlorine, or 1 molecule of hydrogen chloride contains $\frac{1}{2}$ molecule (1 atom) of hydrogen and $\frac{1}{2}$ molecule (1 atom) of chlorine. Hence the formula is HCl. This may be confirmed by a measurement of the density of the gas.

By a careful determination of the limiting density of hydrogen chloride, Gray and Burt (1909) found the molecular weight 36.187 (H = 1). Hence, the atomic weight of chlorine (H = 1) is $36.187 - 1 = 35.187$ or 35.458 (O = 16). By decomposing the gas with heated aluminium they found that 2 vols. gave 1.0079 vols. of hydrogen at S.T.P. The normal density of hydrogen chloride was found to be 1.63915, and with Morley's density of hydrogen 0.089873 this gives for the molecular weight of HCl (H = 1)

$$(1.63915 \times 2) / (0.089873 \times 1.00790) = 36.191,$$

hence Cl = 35.191 (H = 1).

The gravimetric composition of hydrogen chloride was directly determined by Dixon and Edgar (1905), who burnt pure hydrogen from a weighed bulb in which it was absorbed in palladium, in pure chlorine from a bulb of liquid chlorine prepared by the electrolysis of fused silver chloride, and passed into a previously evacuated glass bulb (Fig. 130). The hydrogen was evolved by heating the bulb containing palladium, and kindled in the chlorine by an electric spark. The

* This has occurred in the author's experience.

hydrogen chloride formed was absorbed in water in the bulb and its weight was found. The value $\text{Cl} = 35.458$ ($\text{O} = 16$) was found. Edgar (1908) omitted the water (which gave a little oxygen when chlorine was used in excess), used a quartz apparatus, and condensed and weighed the

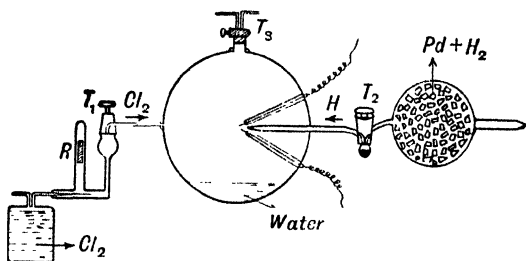


FIG. 130.—Atomic weight of chlorine (Dixon and Edgar).

dry hydrogen chloride in a nickel-plated steel bomb placed in liquid air. The hydrogen, chlorine, and hydrogen chloride were all weighed.

Photochemical union of hydrogen and chlorine.—A mixture of practically equal volumes of hydrogen and chlorine, containing a trace of oxygen, is obtained by the electrolysis of hydrochloric acid (sp. gr. 1.1) with carbon electrodes. The gas is washed with a little water in a bulb-tube and passed through a series of *very thin* glass bulbs (Fig. 131), the

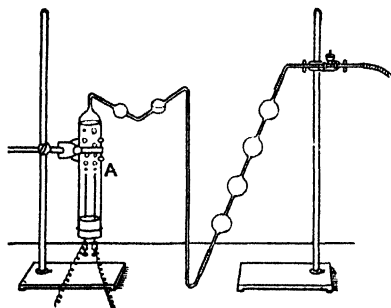


FIG. 131.—Filling glass bulbs with a mixture of chlorine and hydrogen.

operation being performed in a dark room lighted by a ruby lamp. After the gas has passed for at least half an hour, the two ends of the bulbs are closed with wax and the *capillaries* separating them *carefully* sealed off with a small flame. The combustion does not usually spread from the heated part. The bulbs are kept in a dark box.

diluted with nine to fifteen parts of water gives "only a little oxygen with much chlorine at the anode," but Bunsen showed that evolution of oxygen begins to be recognisable with 23 per cent acid; with stronger acids the chlorine is practically pure. With more dilute acids chloric acid is formed at the anode as well as oxygen. The amount of oxygen liberated with 0.1*N* acid is appreciable, according to Haber and Grimberg (1898).

A bulb containing a mixture of hydrogen and chlorine, protected by a plate glass screen (Fig. 132), is exposed to the light of burning magnesium ribbon or flash-powder: a sharp explosion occurs and the glass is shattered. A similar bulb filled with gas dried by passing over P_2O_5 does not usually explode, but the gases combine, as may be shown by opening under litmus solution.

According to Faraday (1833) concentrated hydrochloric acid

The light starts the reaction, which then goes on spontaneously with evolution of heat. Photochemical reactions which involve absorption of energy and stop when the light is cut off, are the formation of ozone from oxygen, and the decomposition of hydrogen chloride and of ammonia, by ultraviolet light.

According to Thos. Thomson, the explosion of a mixture of hydrogen and chlorine on exposure to sunlight was discovered by Dalton, who communicated it to him by letter before the announcement of the similar experiments of Gay-Lussac and Thenard in 1809.

Pringsheim in 1887 found that the mixed gas, when dried with phosphorus pentoxide before passing into the bulb, does not explode when exposed to strong light, but the gases combine completely. Following experiments of H. B. Baker (1894), Coehn and Tramm (1923) found that a carefully purified and dried mixture of hydrogen and chlorine underwent no change on exposure to visible light ($\lambda > 4000$ A.), but a partial pressure of water vapour of 10^{-6} mm. was sufficient to initiate the reaction. With (ultraviolet) light of wave-length smaller than 3000 A. reaction occurred even with very dry gases. Other experimenters report that the rate of combination is not affected by moisture. Dixon and Harker (1890) found that the velocity of the detonation wave in carefully dried hydrogen and chlorine was 1795 m. per sec., and in moist gas it was 1770 m. per sec. Moisture, although assisting the *initiation* of the reaction, appears to retard it once it has begun.

J. W. Draper (1843) investigated and confirmed an effect noticed by Dalton (1809), that a mixture of hydrogen and chlorine did not begin to contract at once when exposed over chlorine water to diffused daylight. There was an initial "hesitation", called the *period of photochemical induction*. Bunsen and Roscoe (1857-59) used the apparatus shown in Fig. 133, called an actinometer. The mixed gases were con-

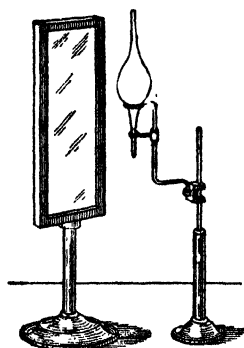


FIG. 132.—Explosion of a mixture of hydrogen and chlorine by exposure to strong light of burning magnesium.

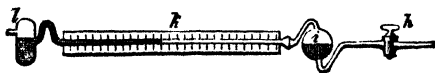


FIG. 133.—Actinometer of Bunsen and Roscoe.

fined in the half-blackened flat bulb *i* by chlorine water. On exposure to light the HCl formed dissolved and the rate of combination was found from the movement of the thread of liquid in the horizontal tube *k*. It was found that the rate of combination was proportional to the intensity of the light. Later experimenters found that with very pure gases free from oxygen the rate of combination is approximately

proportional to the square-root of the light intensity. Bunsen and Roscoe also noticed the photochemical induction period.

Burgess and Chapman (1904) showed that the period of induction was due to traces of impurities such as nitrogen chloride in the chlorine water used to confine the gases, and formed from ammonia or nitrogenous organic matter in the water. If this water was first boiled with chlorine these substances were destroyed, and the gases then began to combine the instant they were exposed to light. Traces of oxygen retard the velocity of combination but do not give rise to a period of induction.

The law of photochemical equivalence.—Planck in 1900 assumed that the energy of light and radiation in general may be absorbed and emitted in definite quanta, the quantum ϵ for each frequency ν being equal to the product of ν and a universal constant h , called **Planck's constant**: $h = 6.6 \times 10^{-27}$ erg seconds, *i.e.* $\epsilon = h\nu$. The smaller the wave-length, the larger the quantum, and light of short wave-length (blue, violet or ultra-violet) is chemically more active than light of longer wave-length (yellow or red). There is reason to believe that a single quantum of light of wave-length 5400 Å. can be detected by a normal eye fully adapted in darkness (Noddack, 1924).

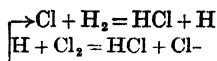
Einstein in 1912 assumed that the *primary process* in a photochemical change is the absorption of one quantum of energy from the radiation by each reacting molecule. This primary process may be followed by changes which occur spontaneously with evolution of energy, so that the yield may exceed, sometimes considerably, that calculated by Einstein's law of photochemical equivalence.

The products of the primary reaction may also undergo a cycle of changes so as to be reproduced, in which case the quantum efficiency would be infinite unless the "chain reaction" is broken at some link by collision with a foreign molecule (*e.g.* oxygen) or with the walls of the vessel. In the union of hydrogen and chlorine, at least a million molecules of hydrogen chloride can be produced per quantum. Nernst suggested the following mechanism:

I. Primary (quantum) reaction (absorbs energy):



II. Secondary reactions:



If the chlorine reacts in the atomic form, the reaction velocity should be proportional to the square-root of the light intensity (since each quantum absorbed produces *two* chlorine atoms), and this result was found with very pure gases free from oxygen (Chapman and Gibbs, 1931).

Taylor and Marshall (1923) found that when atomic hydrogen is added to a mixture of hydrogen and chlorine, more hydrogen chloride than corresponds with its amount is formed.

Atomic chlorine is said to be formed by the action of a high-tension electrodeless discharge in chlorine. It reacts with hydrogen in the dark.

In some reactions photosensitisation occurs. Phosgene, COCl_2 , is a colourless gas absorbing only in the region of the ultraviolet. According to the Grotthuss (1818) and Draper (1841) law only rays which are absorbed are effective in producing chemical change, and phosgene is not decomposed by visible light. If chlorine, which absorbs blue light, is mixed with phosgene and the mixture exposed to ordinary light, the phosgene is decomposed by the energy absorbed by the chlorine, which acts as a photochemical sensitiser: $\text{COCl}_2 = \text{CO} + \text{Cl}_2$. The combination of hydrogen or sulphur dioxide with oxygen is also sensitised by chlorine.

CHAPTER XV

ELECTROLYSIS

Electrolysis.—When an electric current is passed through acidulated water, decomposition into hydrogen and oxygen gases occurs. The process is called **electrolysis**, the acidulated water is called an **electrolyte**, and the platinum plates bringing the current into and out of the solution are called **electrodes**. The electrode connected with the positive pole of the battery is the **positive electrode** or **anode**, that connected with the negative pole is the **negative electrode** or **cathode**. The gases are

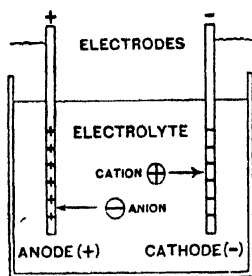


FIG. 134.—Electrolytic cell.

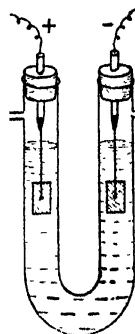


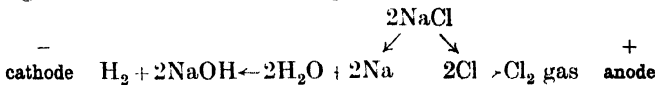
FIG. 135.—U-tube with electrodes.

liberated only at the electrodes. The atom or radical of the electrolyte deposited on the anode is the **negative ion** or **anion**, that deposited on the cathode is the **positive ion** or **cation**. These names are summarised in the diagram in Fig. 134.*

Conductors of electricity are of two kinds : (1) those which conduct the current without undergoing chemical change, and are simply heated by the current ; metals and graphite belong to this class of **metallic conductors** : (2) those which are decomposed by the current, such as acidulated water, and solutions of salts, called **electrolytes**. This name is now also used for the dissolved substances themselves ; common salt and sulphuric acid are called electrolytes because when dissolved in water they form electrolytically conducting solutions.

* It should be remembered that the anode is positive but the anion negative, the cathode negative but the cation positive. The names were invented for Faraday by William Whewell and are not really satisfactory. It is simpler to speak of "positive and negative electrodes" and "positive and negative ions", according to the charges on each.

Concentrated hydrochloric acid is decomposed by electrolysis into hydrogen deposited at the cathode and chlorine deposited at the anode. Fused sodium chloride is decomposed into metallic sodium at the cathode and chlorine gas at the anode. With a solution of sodium chloride it may be supposed that the sodium first deposited on the cathode by a primary action (*i.e.* as a direct result of electrolysis) at once reacts with the water by a secondary action (*i.e.* one not involving electrolysis), forming a solution of sodium hydroxide and liberating hydrogen gas. Chlorine is evolved by a primary action at the anode, the discharged chlorine atoms combining to form molecules of chlorine gas :



Red litmus solution is turned blue around the cathode by the alkali and is bleached around the anode by the chlorine (Fig. 135).

The primary deposition of sodium may be shown at a cathode of mercury (Fig. 136), when sodium amalgam will be formed and very little hydrogen evolved.

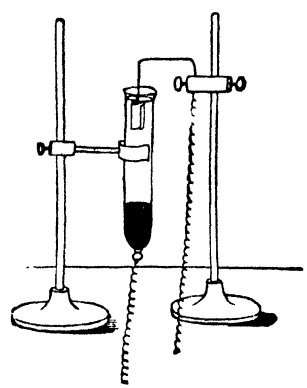
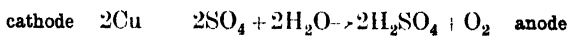
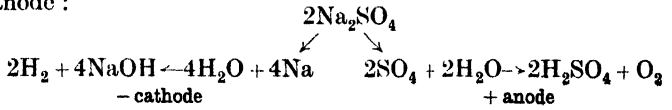


Fig. 136 ---Electrolysis with a mercury cathode.

When a solution of copper sulphate is electrolysed with platinum electrodes there is a deposit of red metallic copper on the cathode but no gas. At the anode sulphuric acid accumulates and oxygen gas is evolved. The CuSO_4 gives metallic copper Cu on the cathode, and the SO_4 radical at the anode. The SO_4 reacts with water by a secondary action to form oxygen gas, and a solution of sulphuric acid :



A solution of sodium sulphate on electrolysis gives sodium hydroxide and hydrogen gas at the cathode, and sulphuric acid and oxygen gas at the anode :



The production of acid and alkali may be shown by adding purple litmus to the solution of sodium sulphate and electrolysing in the U-tube with platinum electrodes (Fig. 135). The litmus is turned blue

by the alkali at the cathode and red by the acid at the anode. The hydrogen and oxygen gases evolved may be collected over water through the side tubes and tested.

The distinction between primary and secondary products of electrolysis was made by Faraday in 1833. Faraday thought that acids and bases from oxysalts (*e.g.* Na_2O and SO_3 from Na_2SO_4) were primary products, and metals (*e.g.* copper) were secondary products formed by reduction by nascent hydrogen, but Daniell (1839) followed Davy (1815) in taking the metals and acid radicals (*e.g.* SO_4) as primary products.

Although the theory of secondary reactions gives a plausible explanation of the formation of hydrogen and oxygen in the electrolysis of many salt solutions, yet the reactions are probably more direct. The current is carried through the solution by the ions of the salt, *e.g.* 2Na and SO_4 , which accumulate round the electrodes. These are not discharged on the electrodes, since the hydrogen and hydroxide ions of the water are more easily discharged ($\text{H}_2\text{O} = \text{H} + \text{OH}$). The hydrogen ion is discharged at the cathode to form hydrogen gas, leaving the hydroxide ion to form sodium hydroxide with the sodium ion which had moved to the cathode. The hydroxide ions are discharged and decompose into oxygen gas and water at the anode, leaving the hydrogen ions of the water to form sulphuric acid with the sulphate ion which had moved to the anode: $4\text{OH} = \text{O}_2 + 2\text{H}_2\text{O}$ (see p. 241).

Faraday's laws of electrolysis.—The first systematic investigations of electrolysis were carried out by Humphry Davy and were continued *quantitatively* by his pupil and assistant Faraday, who in 1832–33 discovered two important laws of electrolysis.

Faraday measured the quantity of electricity passing through the electrolytes by means of a water voltmeter (p. 41), and the modern definition of the unit quantity of electricity is also based on its electrochemical action (p. 223).

The quantity of electricity which passes round a circuit is measured by the current strength multiplied by the time. The current

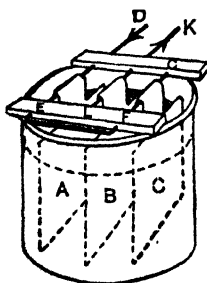


FIG. 137.—Copper coulometer.

strength is measured in amperes; one ampere passing for one second corresponds with unit quantity of electricity, or one coulomb. If the current passes until 1.008 gm. of hydrogen is liberated from the acidulated water, 96,500 coulombs pass through the cell. If this passes as a small current for a long time (*e.g.* 0.1 ampere for 965,000 sec.) or as a large current for a shorter time (*e.g.* 10 amperes for 9,650 sec.) the result is the same. Faraday showed by experiments (see below) that this holds generally for electrolytes, and also that it applies to the case where

an ion is formed, not deposited, at an electrode, *e.g.* when copper dissolves from a copper anode in copper sulphate solution. Hence:

The weight of an ion deposited or formed at an electrode is proportional to the quantity of electricity which passes through the electrolyte.

This is Faraday's First Law of Electrolysis (1832); he stated it in the form: "*the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.*"

This may be tested by finding the weight of copper deposited in a copper voltameter (or coulometer) (Fig. 137) by a steady current in a given time. The copper coulometer consists of two sheet copper anodes *A* and



MICHAEL FARADAY.

C hanging from a bent copper rod *DEFG* supported in two wooden strips, and a thin sheet copper cathode *B*, supported from the copper rod *KL*. The cathode is weighed and the vessel filled with copper sulphate solution. A current of not more than 1/50 amp. per sq. cm. of cathode surface is passed by inserting a suitable resistance and a current-measuring instrument in series with the coulometer and a battery. After a suitable time the cathode is taken out, washed, dried and weighed to find the weight of copper deposited. The experiment is repeated with the same current but twice the time, when twice as much copper will be deposited as in the first experiment. Keeping the time the same as in the first experiment, the current strength is now reduced to half by a suitable resistance in

series, when the weight of copper deposited will be half the previous weight.

By comparing the weights of different ions deposited (or formed) by the same current passing through two or more electrolytic cells in series, Faraday established another important result :

The weights of different ions deposited or formed by the same quantity of electricity are in the ratios of their chemical equivalents.

This is Faraday's Second Law of Electrolysis (1833) : he stated it in the form : " *electro-chemical equivalents coincide, and are the same, with ordinary chemical equivalents.*" If the quantity of electricity is 96,500 coulombs, the law is more concisely expressed in the form : 96,500 coulombs deposit or form one gram-equivalent of any ion in electrolysis. This quantity of electricity is called a faraday and denoted by F.*

The ampere is defined as that current which, flowing uniformly for 1 second, deposits under specified conditions 0.001118 grams of silver from a solution of silver nitrate. This is called the electrochemical equivalent of silver. The weight z gm. of any ion deposited by 1 coulomb is its electrochemical equivalent ; hence the weight deposited by a uniform current of C amperes flowing for t seconds is :

$$W = C't.$$

(What Faraday called the " electro-chemical equivalent " is what is now called the chemical equivalent). Since the chemical equivalent of silver (which is the same as its atomic weight) is 107.880, the quantity of electricity required to deposit this will be $107.880/0.001118 = 96,500$ coulombs.

Faradays' second law may be tested by passing the same current through three cells in series containing : (i) acidulated water in a water voltmeter ; (ii) copper sulphate solution with copper electrodes in a copper coulometer ; and (iii) a solution of silver nitrate

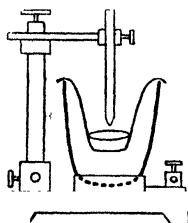


FIG. 138.—Silver coulometer.

in a silver coulometer. The silver coulometer (Fig. 138) consists of a platinum crucible, which is carefully weighed and contains a 30 per cent solution of silver nitrate. The crucible is placed on a brass plate, which is the negative terminal. The anode is a rod of pure silver suspended in the solution. A small glass cup is suspended under the anode to retain detached pieces. The crystalline deposit of silver is washed with water and alcohol, and the crucible is dried in an air-oven* and weighed. The volumes of hydrogen and

oxygen, and the weights of copper and silver deposited, are found. The weights should be in the ratio of the equivalents, viz. 1.008, 8, 31.5 and 107.9.

* Not to be confused with the farad, the unit of electrical capacity.

Faraday's second law provides a method of finding the equivalent of an element; for example, the equivalents of copper and silver could be determined in the experiment described.

Faraday's laws apply also to *fused electrolytes*. If an electrolytic circuit includes a water voltameter, a copper coulometer, and a cell containing fused silver chloride with a carbon anode (Fig. 139), the volumes of hydrogen and oxygen liberated from the water, and the weights of copper and silver deposited from the copper sulphate solution and the fused silver chloride may be found. The weights of hydrogen, oxygen, copper and silver liberated will be found to be in the ratio of the chemical equivalents,

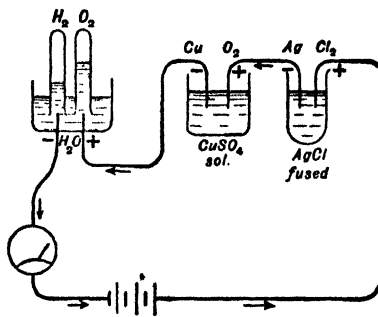


FIG. 139.—Diagram of electrolytic circuit.

1, 8, 31.5, and 108.

Faraday used fused stannous chloride, which was decomposed into tin and chlorine, but the chlorine at once combined with stannous chloride to form stannic chloride, which volatilised. He found that 3.2 grains of tin were set free by the same current which liberated 3.85 cubic inches of electrolytic gas in a voltameter (he does not specify temperature and pressure), and hence he calculated the equivalent of tin as 57.9 instead of 58 found by the chemical method (modern value = 59 when $H = 1$). Faraday also used fused lead chloride with a carbon anode, from which chlorine was evolved. Fused silver chloride gave him trouble because the silver crystals grew across to the anode and short-circuited the current.

He showed with fused lead chloride and two molten lead electrodes that the weight of lead deposited on one electrode was equal to the loss in weight of the other electrode owing to the formation of lead chloride by the action of the liberated chlorine. Both weights of lead were equivalent to the water decomposed in a water voltameter. With fused silver chloride and two silver electrodes, the loss in weight of the silver anode was equal to the weight of silver deposited on the cathode, which was withdrawn as the silver crystals grew upon it.

The theory of electrolysis.—Since the ions appear only at the electrodes it is simplest to assume that they are charged atoms or radicals, the sign of the charge of an ion being *opposite* to that of the electrode towards which it moves by attraction. Thus :

Anions are negatively charged atoms or radicals and cations are positively charged atoms or radicals.

The electricity is ferried across from one electrode to the other by the charged ions, and this electrolytic current completes that passing through the metallic circuit outside the electrolytic cell. *The strength of*

the current is uniform throughout the whole circuit, whether the latter is all metallic or is composed of metal wires and electrolytes. Since the current in the electrolyte is carried solely by charged ions, the weight of an ion moving to an electrode in a given time is proportional to the current strength, i.e. to the quantity of electricity passing through the electrolyte. This is Faraday's First Law of Electrolysis.

Faraday's Second Law of Electrolysis is explained by assuming that :

The electric charge of an ion is the same for all ions of the same valency and is proportional to the valency.

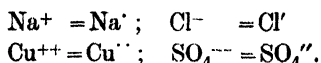
Thus, a univalent cation such as sodium carries unit positive charge ; a bivalent cation such as copper carries 2 unit positive charges ; a univalent anion such as chlorine carries a unit negative charge equal but opposite to the unit positive charge on the sodium ion ; a bivalent negative ion such as SO_4 carries 2 unit negative charges. In general, if e is the unit charge then the charge carried by an ion of valency n is $\pm ne$, positive or negative. A positive charge carried in one direction is equivalent to an equal negative charge carried in the opposite direction. The charge on a gm. at. or gm. mol. weight of an ion is Nne , where N is Avogadro's number, and on one equivalent weight the charge is Ne . Hence : $Ne = F$.

When the charge Ne passes round the circuit it carries in the electrolyte weights of ions equal to their atomic or molecular weights divided by the valency n , and deposits them on the electrodes. Hence the same quantity of electricity deposits weights of ions in the ratios of their equivalents. This is Faraday's Second Law.*

The electron.—The constant electric charge on univalent ions and the simple multiple relation between the charges on multivalent ions suggest that electricity like matter is divided into atoms. This was suggested by Maxwell in 1873, with some reserve, and in 1874 G. J. Stoney calculated this unit charge, which he later called an electron. Helmholtz in 1881 said : "The most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also is divided into definite elementary portions, which behave like atoms of electricity." The *free* atom of electricity is the *negative* electron, and an atom which has gained one electron has unit negative charge, whilst an atom which has lost one electron has unit positive charge. The hydrogen atom, the lightest atom, loses one electron to form the positively charged **proton**. The mass of the electron, determined by J. J. Thomson in 1897 (p. 381), is only about 1/1840 that of the hydrogen atom or proton.

* It must not be thought that Faraday gave this explanation : his ideas are not easy to understand and the present theory is due to Helmholtz.

For convenience, the + or - charge of an ion is often represented by a dot or a dash :



The ionic charges are large. To liberate 1 gm. of hydrogen, the current which lights an electric lamp (0.5 amp.) would have to pass for nearly fifty-four hours. If charges equal to that associated with 1 mgm. of hydrogen could be given to each of two small metal spheres placed 1 cm. apart, they would repel each other with a force of about 10^{14} tons weight. As Faraday remarked, the electric charges concerned in the most violent flash of lightning would barely serve to decompose a single drop of water.

Theory of electrolytic dissociation.—All experiments on electrolysis can be explained by the simple assumption that *the ions move independently in electrolytes*.

Since any applied E.M.F., however small, will produce electrolysis if polarisation (which opposes the electrolysing E.M.F.) is eliminated, it seems that no work is spent in breaking up the electrolyte molecules. Clausius in 1857 assumed that some of these are already broken up in the solution and the only action of the current is to guide the free charged ions to the electrodes. Since the dissociation of common salt into sodium and chlorine in solution seemed inconsistent with ordinary chemistry, Clausius assumed that only very few molecules were ionised, this process going further as the ions are removed. A similar idea had been put forward for chemical reactions generally by Williamson in 1851.

In 1887 Arrhenius gave reasons for supposing that nearly all the molecules of an electrolyte are dissociated in solution into charged ions. In electrolysis the ions move with the current, which in the solution consists only of the moving ions. In a solution of sodium chloride the salt exists as sodium ions Na^+ and chloride ions Cl^- .

When a Cl^- ion reaches the anode it gives up an electron e to the metal electrode and forms a chlorine atom: $\text{Cl}^- = \text{Cl} + e$. The electron passes round the metal circuit outside the cell, and an electron from the cathode is given to a Na^+ ion, so neutralising its charge and forming a sodium atom: $\text{Na}^+ + e = \text{Na}$. The Cl atoms at the anode form Cl_2 molecules and the Na atoms at the cathode either dissolve in mercury if the cathode is of mercury, or react with water to form sodium hydroxide and hydrogen if the cathode is of platinum.

It should be noted that the sum of the charges on the cations in a solution must always equal the sum of the charges on the anions, since the whole solution is uncharged; e.g. Cu^{++} and SO_4^{--} and 2 Na^+ and SO_4^{--} .

The electronic charge.—The charge on the electron has been determined in different ways, notably by R. A. Millikan (1912), who used the following very direct method.

Two metal plates, separated by a distance of about 1 mm., were charged positively and negatively by attaching them to the poles of a battery. Into the air above the plates a fine dust of pulverised oil was blown by a spray. The oil drops, which settled very slowly on account of their small size, were electrically charged by exposure to X-rays. A particular drop, falling between the plates through a small hole in the upper plate, was focused in the field of a microscope with a scale in the eyepiece, as shown diagrammatically in Fig. 140. By varying the potential difference between the plates,

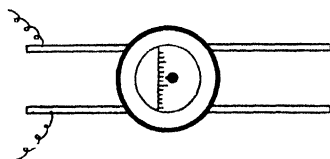


FIG. 140.—Millikan's determination of the electronic charge.

the charged drop could be made to move upwards or downwards with any desired velocity. From the ratio of the velocities with and without the potential difference, the charge on the drop could be calculated.

It was found that this charge varied during an experiment. The variations were not continuous, but took place in jumps. Each sudden change was assumed to correspond with the gain or loss of one or more electrons by the drop, and it was found that the charge varied in small multiples of 1.6×10^{-19} coulombs. Thus, *the negative charge on the electron is $e = 1.6 \times 10^{-19}$ coulombs.*

The value of the electronic charge can be determined in other ways. If N is Avogadro's number, then $F = Ne$, where F is the faraday; hence any determination of N will give a value of e .

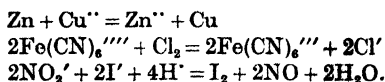
The nature of the ions.—The question was asked Arrhenius as to how it is possible to have in a solution of common salt either free sodium or free chlorine, since the former is violently attacked by water, and the latter is a greenish-yellow gas, forming a greenish-yellow solution with water. The solution shows none of the properties of sodium or chlorine. The answer is that neither metallic sodium nor chlorinic gas is assumed to be present but only sodium ions and chloride ions. These differ from the free elements by having large electric charges.

Ferrous and ferric salts in solution show quite different reactions, and they show none of the properties of metallic iron, except in being slightly magnetic. They are, on the present theory, considered as giving two different ions in solution, viz. the ferrous ion Fe^{2+} , and the ferric ion Fe^{3+} . The addition of unit positive charge alters the properties of the ferrous ion, and it is reasonable to suppose that the properties of sodium and chlorine atoms are also changed by the assumption of charges. Metallic sodium and iron may be regarded as discharged ions, having zero charges, Na° and Fe° .

The *electrovalency* of an ion is equal to its charge; +3 for the ferric ion Fe^{+++} , -4 for the ferrocyanide ion $Fe(CN)_6^{----}$. It represents the number of electrons lost or gained by a neutral atom or radical in forming a cation or anion, respectively. This is an extension of the

elementary idea of valency, since sodium chloride in solution is not $\text{Na}-\text{Cl}$ but Na^+ and Cl^- , two separate ions.

Reactions between ions.—Since most salts are ionised in solution, the reactions between them usually occur between ions. On adding sodium chloride solution to silver nitrate solution, the free silver ion and free chloride ion form insoluble silver chloride, which is precipitated, whilst the free sodium and nitrate ions take no part in the reaction. Instead of the equation: $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$, a more correct representation is: $\text{Ag}^+ + \text{NO}_3^- + \text{Na}^+ + \text{Cl}^- = \text{AgCl} + \text{Na}^+ + \text{NO}_3^-$, or since the sodium and nitrate ions are not concerned, the ionic equation: $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}$. In an ionic equation the sum of the positive and negative ionic charges must be the same on both sides:



Oxidation and reduction.—Oxidation and reduction reactions usually involve *changes of valency*; in stannous oxide SnO tin is bivalent, in stannic oxide SnO_2 it is quadrivalent, and in ferrous oxide FeO and ferric oxide Fe_2O_3 iron is bivalent and trivalent, respectively. The oxysalts were represented on the old dualistic theory of Berzelius as compounds of basic oxides of the metals and acidic oxides (acid anhydrides): ferrous sulphate $\text{FeSO}_4 = \text{FeO}, \text{SO}_3$; ferric sulphate $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3, 3\text{SO}_3$. Stannous and ferrous chlorides are also said to be oxidised to stannic and ferric chlorides by the reactions $\text{SnCl}_2 + 2\text{Cl} = \text{SnCl}_4$, and $\text{FeCl}_2 + \text{Cl} = \text{FeCl}_3$, the valency of tin increasing from 2 to 4 and that of iron from 2 to 3. The reverse changes are examples of reduction.

In the case of ions, it is seen that oxidation is an increase of positive charge of a cation or increase of positive electrovalency, *e.g.* Fe^{++} becomes Fe^{+++} , and reduction is decrease of positive cation charge or positive electrovalency. In the case of anions, decrease of negative charge or decrease of negative electrovalency corresponds to oxidation, and increase of negative charge or increase of negative electrovalency to reduction: ferrocyanide ion $\text{Fe}(\text{CN})_6^{''''}$ is oxidised to ferricyanide ion $\text{Fe}(\text{CN})_6^{''''}$, manganate ion $\text{MnO}_4^{''}$ is oxidised to permanganate ion MnO_4^+ . Changes of principal valency of the metal atom in the ion occur here; bivalent iron in $\text{Fe}(\text{CN})_6^{''''}$ becomes trivalent iron in $\text{Fe}(\text{CN})_6^{''''}$, and 6-valent manganese in $\text{MnO}_4^{''}$ becomes 7-valent manganese in MnO_4^+ . If the principal valency of the metal atom is taken as positive, that of oxygen, halogens, and negative radicals as negative, the ionic charges may be found:

$\text{Fe}(\text{CN})_6^{''''}$: ferrous iron Fe^{II} , +2, cyanide radical CN , -1, \therefore the valency of the ion is +2 - 6 = -4.

$\text{Fe}(\text{CN})_6^{''''}$: ferric iron Fe^{III} , +3, \therefore the valency of the ion is 3 - 6 = -3.

Since the net charge must remain constant in an ionic reaction, oxidation and reduction must occur simultaneously, some substances being oxidised and others reduced in the reaction.

Equivalent conductivity.—In a cell containing two platinum electrodes 1 sq. cm. in area placed parallel to each other at a distance of 1 cm. apart, the current in amperes which passes through a solution of an electrolyte between the plates when the latter are at a difference of potential of 1 volt is called the **conductivity** (sometimes **specific conductivity**) of the solution, denoted by κ .

The conductance of a cylinder of material of length l cm. and cross-section s sq. cm. and resistance R ohms is

$$\frac{1}{R} = \frac{\kappa s}{l} \text{ ohm}^{-1}.$$

Since s has the dimensions (cm.)² and l cm., the dimensions of κ are ohm⁻¹ cm.⁻²

$$\kappa = \frac{1}{R} \frac{l}{s}.$$

When a solution of a partly ionised electrolyte is diluted the conductivity κ decreases because there are fewer ions per cm.³ but the degree of ionisation α increases with dilution, since more undissociated molecules ionise.

Let a volume ϕ cm.³ of solution containing 1 gram equivalent of electrolyte be poured into a cell with parallel electrodes of any size which are 1 cm. apart (Fig. 141). The current in amperes passing when the potential difference between the electrodes

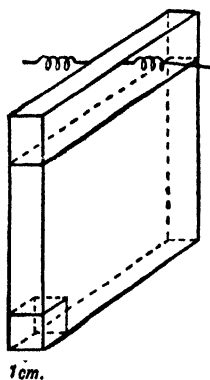


FIG. 141.—Equivalent conductivity.

is 1 volt is defined as the **equivalent conductivity** λ or Λ . Since the solution contains ϕ unit cubes in parallel between the electrodes, the current is ϕ times the conductivity κ , hence :

$$\lambda = \phi \kappa.$$

If η is the concentration in gm. equiv. per cm.³

$$\eta = 1/\phi; \therefore \lambda = \kappa/\eta.$$

As the volume ϕ containing 1 gm. equiv. increases, λ increases and approaches a constant **limiting value** λ_∞ called the **equivalent conductivity at infinite dilution**. Since the concentration then approaches zero, λ_∞ is also denoted by λ_0 , the **equivalent conductivity at zero concentration**. The dimensions of λ are those of κ divided by (equiv./cm.³), i.e. ohm⁻¹ cm.² equiv.⁻¹

The approach of the equivalent conductivity λ to the limiting value λ_∞ at infinite dilution can be explained in two ways. (1) It may be assumed that the electrolyte is completely dissociated into ions at all concentrations, but the speeds of the ions increase as the solution

becomes more dilute, until in very dilute solution the ionic speeds (for a given potential gradient between the electrodes) become constant. Or, (2) it may be assumed that the speeds of the ions are practically constant at the various concentrations but the dissolved electrolyte is incompletely ionised, the ionisation increasing with dilution until at very high dilutions the electrolyte is completely ionised.

On the second assumption the ratio of the equivalent conductivity λ_v at any dilution v to that at infinite dilution λ_∞ , when all the electrolyte is ionised, gives the degree of ionisation α at the given dilution : $\lambda_v/\lambda_\infty = \alpha$.

The dilution is the reciprocal of concentration, *i.e.* v is the number of ml. containing 1 gm. equivalent of total electrolyte. In practice, the concentration is usually measured in gm. equiv. per litre and the dilution ϕ in litres per gm. equiv.

Electrolytes such as acetic acid which are only slightly ionised in solution are called **weak electrolytes**, *e.g.* acetic acid :



and their degree of ionisation is given by the ratio $\alpha = \lambda_v/\lambda_\infty$.

Electrolytes such as hydrochloric acid which are largely ionised in solution (over 90 per cent) are called **strong electrolytes**, and some are now regarded as completely ionised. On account of the electrical interaction of the oppositely charged ions the change of equivalent conductivity on dilution is in this case due almost entirely to changes in ionic speed, and the ratio λ_v/λ_∞ no longer measures the degree of ionisation, which is practically 1.

Determination of conductivity.—If a direct current from a battery is passed between platinum electrodes in a solution of an electrolyte, the current strength may decrease as electrolysis proceeds. This is partly due to the accumulation of the products of electrolysis at the electrodes. These form a galvanic cell which tends to send a current in the opposite direction to that driven round the circuit by the battery. This reverse electromotive force, tending to oppose the direct electromotive force causing electrolysis, is called the **electromotive force of polarisation**.

In measurements of the conductivity of electrolytes it is necessary to eliminate polarisation. F. W. Kohlrausch (1869) used an *alternating current*, *i.e.* one which flows alternately in one direction and then in the other, with a very small time interval between the reversals of direction. Such a current is supplied by an induction coil. The ions are driven first in one direction and then in the other, and only very small amounts are deposited on the electrodes.

Polarisation is further reduced by depositing platinum black on the electrodes, by electrolysing between them a solution of 1 gm. of chloroplatinic acid and 8 mgm. of lead acetate in 30 ml. of water, with an accumulator, and reversing the current from time to time. The platinum black exposes a large surface.

The electrolytic or conductivity cell is shown in Fig. 142. The platinum wires attached to the horizontal platinised platinum foil electrodes are

sealed into mercury contacts, from which copper wires are taken to a Wheatstone bridge arrangement shown diagrammatically in Fig. 143: r is the electrolytic cell and R a resistance box, a metre wire bridge with a sliding contact being connected with the coil and telephone as shown. The telephone is used as a detector of alternating current and the bridge is balanced when the sound in the telephone is a minimum. The cell should be in a thermostat of constant temperature, since the conductivity increases rather considerably with temperature. The temperature coefficient of the equivalent conductivity $(1/\lambda)(d\lambda/dt)$ is about 2 per cent per degree, so that the temperature should be constant to 0.01° . Measurements are usually made at 18° or 25° .

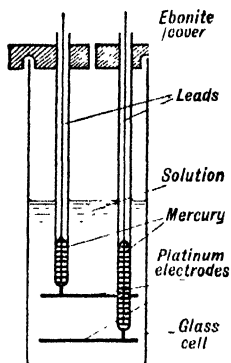


FIG. 142.—Conductivity cell.

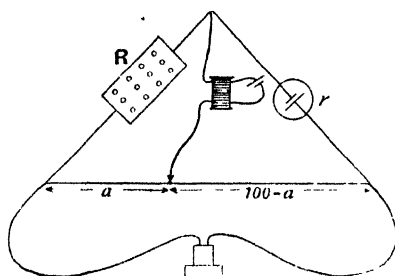


FIG. 143.—Diagram of conductivity apparatus.

The resistance of the conductivity cell is given by the Wheatstone bridge formula: $\frac{R}{r} = \frac{a}{100-a}$; $\therefore r = R \times \frac{100-a}{a}$ ohms. Ohm's law has been proved experimentally to apply to electrolytes. The conductance is $1/r$, i.e. the current in amperes for 1 volt potential difference between the electrodes.

The electrodes of the conductivity cell will not usually be exactly 1 sq. cm. in area, parallel, and 1 cm. apart, so that the conductance $1/r$ is not usually equal to the conductivity κ . Since the relation between the two depends only on the dimensions of the cell, it is possible to determine this once for all by using as electrolyte a solution of known conductivity, viz. a normal solution of potassium chloride (74.555 gm. of pure KCl, weighed in air, in 1 litre of solution) for which at 18° $\kappa_{18^\circ} = 0.09822$. If the resistance of the cell containing this solution is r , $\kappa_{18^\circ} = C/r = 0.09822$, where C is the cell constant. If any other solution is used, and if the resistance is r' ohms, the conductivity is $\kappa'_{18^\circ} = C/r'$.

In Fig. 144 the values of the equivalent conductivities λ for several electrolytes are plotted against the square-roots of the concentrations of the solutions in gm. equiv. per litre. The approach to a limiting value λ_0 for zero concentration (or infinite dilution) is seen. The dotted straight lines are from the theoretical equation (p. 240), and it is seen

that the observed points (shown on the full lines) approach the theoretical lines at infinite dilution.

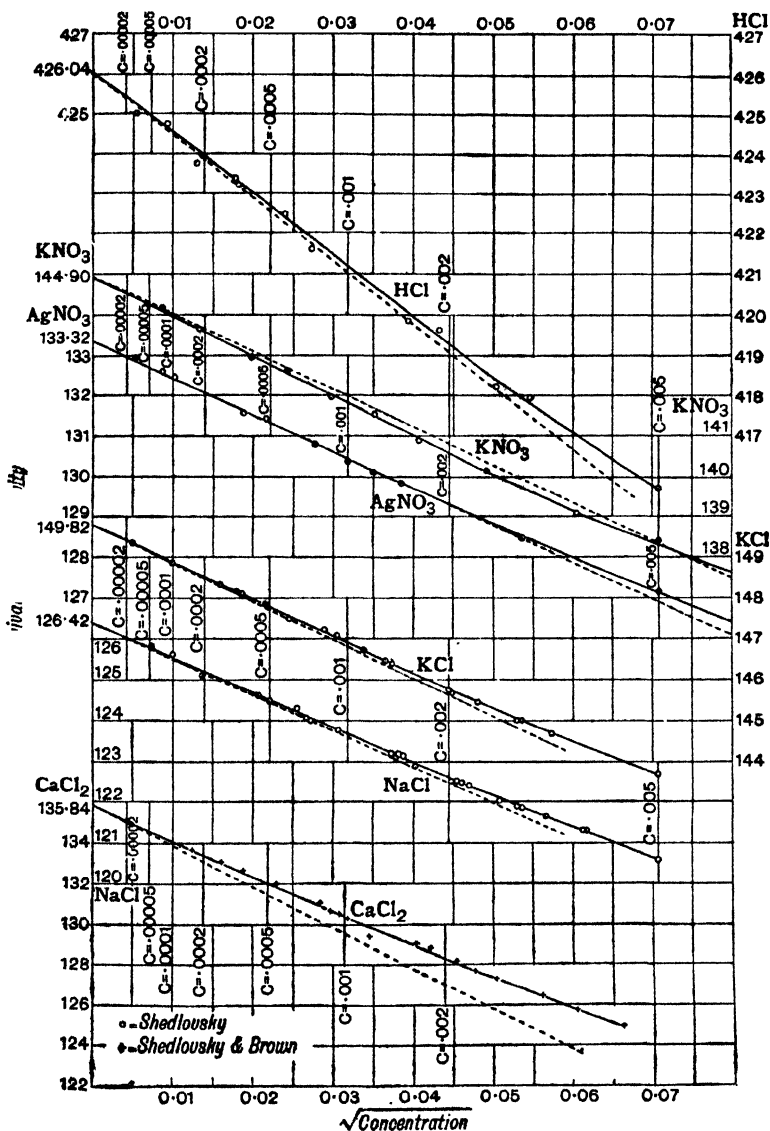


FIG. 144.—Equivalent conductivities of electrolytes.

Reproduced (with modification) from McKenna's "Theoretical Electrochemistry" (Macmillan.)

Kohlrausch's law.—The independent movement of the ions of an electrolyte in dilute solution which is assumed in the theory of

electrolytic dissociation gives a simple explanation of a result discovered experimentally by Kohlrausch in 1875 and known as **Kohlrausch's law**: *the equivalent conductivity of an electrolyte at infinite dilution is the sum of two parts, one depending only on the cation and the other only on the anion*:

$$\lambda_{\infty} = l_c + l_a,$$

where l_c and l_a are called the **mobilities** of the ions expressed in equivalent conductivity units ($\text{ohm}^{-1} \text{cm.}^2 \text{equiv.}^{-1}$). This is illustrated by the figures for λ_{∞} at 18° for four salts, the differences being constant:

$$21.1 \left\{ \begin{array}{l} \text{KCl} \quad \begin{array}{l} 130.0 \\ -3.7 \\ \hline 126.3 \end{array} \\ \text{NaCl} \quad \begin{array}{l} -3.7 \\ -108.9 \\ \hline 105.2 \end{array} \\ \text{KNO}_3 \\ \text{NaNO}_3 \end{array} \right\} 21.1$$

Clearly, $21.1 = l_{\text{K}} - l_{\text{Na}}$, and $3.7 = l_{\text{Cl}} - l_{\text{NO}_3}$.

In order to calculate the separate values of l_c and l_a use is made of the *transport number*, determined as explained below.

MOBILITIES IN AQUEOUS SOLUTION AT 18° .

Cations l_c .		Anions l_a .	
Na'	43.3	Cl'	65.3
K'	64.5	Br'	67.3
NH ₄ '	64.5	I'	66.1
H'	315.6	NO ₃ '	61.6
Ag'	54.0	OH'	174
$\frac{1}{2}$ Zn''	46.7	CH ₃ COO'	35
$\frac{1}{2}$ Cu''	45.5	$\frac{1}{2}$ SO ₄ ''	67.9
$\frac{1}{2}$ Ba''	55.0	$\frac{1}{2}$ CO ₃ ''	60

The large mobilities of the hydrogen and hydroxide ions should be noted.

The value of λ_{∞} for a weak acid, such as acetic acid at 18° , is found by adding 315.6, the mobility of the hydrogen ion, to the mobility of the anion, *e.g.* 35 for the acetate ion, CH₃COO',

$$\therefore \lambda_{\infty} \text{ for acetic acid} = 315.6 + 35 = 350.6.$$

The specific conductivity κ of saturated silver chloride solution at 18° after suitable correction by subtraction of the conductivity of the water used, is $1.24 \times 10^{-3} \text{ ohm}^{-1} \text{cm.}^{-1}$, and since the solution is very dilute the silver chloride may be considered as completely ionised. Now $\lambda = \kappa/\eta$, and in this case λ may be taken as $\lambda_{\infty} = 54.0 + 65.3 = 119.3$; $\therefore \eta = 1.24 \times 10^{-3} / 1.193 \times 10^2 = 1.04 \times 10^{-5} \text{ equiv. per cm.}^3$

Migration of ions.—The bodily transfer of an ion under the influence of an electric field can be demonstrated, and its speed measured, by Nernst's apparatus shown in Fig. 145.

The U-tube is half-filled with a solution containing 0.3 gm. of KNO₃ in a litre of water. By connecting a funnel with the capillary tap below the

U-tube, a solution containing 0.5 gm. of KMnO_4 per litre of water, to each 100 ml. of which 5 gm. of urea have been added to increase its density, is slowly admitted. The surface of separation between the liquids should be sharp. A current of 0.3–0.4 amp. is passed between the platinum electrodes from D.C. mains. The purple MnO_4^- ions move towards the anode, and the levels alter as shown. If the initial levels are marked by thin strips of gummed label, the change is apparent after 10–15 minutes.

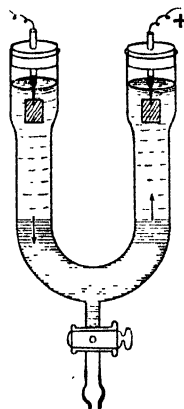


FIG. 145.—Demonstration of ionic migration.

This experiment shows that the speed of the ions in bulk through the solution is very slow, as in the diffusion of dissolved substances (p. 118). In both cases the moving particles enter repeatedly into collision with the solvent molecules. The actual ionic velocities under a potential gradient of 1 volt per cm. (for very dilute solutions, where the influence of the ions on one another may be neglected) are of the order of 0.001 cm. per sec.

The ions in their motion in a very dilute solution are under the influence of two forces: (i) the *driving force* of the potential gradient; (ii) the *frictional resistance* of the solvent. The frictional resistance is enormous. In order to pull 1 gm. mol. of potassium ions through the solution with a speed of 1 cm. per sec. it would be necessary to apply to them an aggregate force of 1,500,000 tons (Kohlrausch).

The unequal speeds of different ions moving through an electrolyte in the same potential gradient give rise to changes of concentration of *electrolyte* (not ions separately) around the electrodes. These changes were noticed by Gmelin in 1838 and by Daniell and Miller in 1843, but were first fully investigated and related to the ionic velocities by Hittorf (1853). In Fig. 146 the black and white circles represent the cations and anions, in the upper row *a* before electrolysis and in the lower row *b* after. The black circles move to the left with a speed *u* and the white circles to the right with a speed *v* which, in the

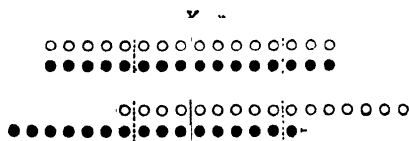


FIG. 146.—Migration of ions.

case considered, is twice as great as *u*. The vertical line *xy* divides the original arrangement into two equal parts.

Before electrolysis there are eight black and white ions on each side. After electrolysis, when six equivalents of electrolyte have been decomposed and the unpaired ions deposited, there are four undecomposed equivalents of electrolyte on the left and six on the right, so that four equivalents of electrolyte have been lost on the left and two on the right. *The losses of neutral electrolyte around the electrodes are in the ratio of the speeds of the ions migrating away from the electrodes.*

Transport number.—The fractions of the total current carried by the cation and anion in the above example are one third and two thirds, respectively, or generally

$$u/(u+v) \quad \text{and} \quad v/(u+v)$$

and since by Kohlrausch's law the total current λ_∞ is the sum of l_c and l_a :

$$l_c/\lambda_\infty = u/(u+v) \quad \text{and} \quad l_a/\lambda_\infty = v/(u+v) \dots\dots\dots(1)$$

The fraction of the total current carried by one ion is called its **transport (or transference) number, n** . It is not a constant depending only on that ion (as the mobility is) but varies according to the mobility of the other ion. If n_c and n_a are the transport numbers of the cation and anion, respectively :

$$l_c/l_a = n_c/n_a \dots\dots\dots(2)$$

Since the two ions carry all the current

$$n_c + n_a = 1. \dots\dots\dots(3)$$

From equation (2) and Kohlrausch's law :

$$\lambda_\infty = l_c + l_a$$

it is possible to calculate l_c and l_a separately from the value of λ_∞ and either n_c or n_a (the other being given by equation 3).

Determination of transport number.—An apparatus used for the determination of the transport number for silver nitrate is shown in Fig.

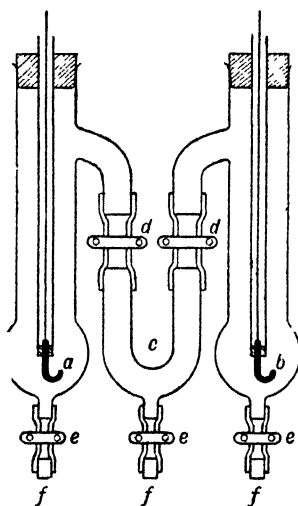


FIG. 147.—Determination of transport number.

147. The three glass parts are connected by rubber tubing. The anode a and cathode b are of thick silver wire cemented into glass tubes and the whole is filled with silver nitrate solution of known concentration and placed in a thermostat. While the apparatus is in the thermostat the rubber tubes are closed by pieces of glass rod f . A current of 0.02–0.04 amp. is passed for $1\frac{1}{2}$ –3 hours. The experiment must be stopped before any change has occurred in the middle part c of the solution, and the current must not be large enough to cause heating and consequent mixing of the solutions in the different parts by convection. A silver coulometer in series measures the total quantity of electricity passed. After the experiment

the screw clips d, d are closed, the apparatus taken out of the thermostat, and the liquid in the anode compartment removed through e , the compartment being washed out with some of the original solution and

the total liquid weighed and analysed. The liquid in the U-tube is run out and analysed to make sure that its composition is unchanged.

An experiment gave the following results : 1 gm. of original solution contained 0.001136 gm. Ag or 0.001788 g. AgNO_3 and $1 - 0.001788 = 0.9982$ gm. water. After electrolysis 20.09 gm. of anode liquid contained 0.03955 gm. Ag or 0.06227 gm. AgNO_3 and $20.09 - 0.06227 = 20.03$ gm. water. The original solution contained

$$0.001136 \times 20.03 / 0.9982 = 0.02280 \text{ gm. Ag}$$

to 20.03 gm. water. \therefore Ag in anode compartment has increased by

$$0.03955 - 0.02280 = 0.01675 \text{ gm. Ag.}$$

In the silver coulometer 0.0322 gm. Ag deposited and the same weight must have dissolved from the anode, hence the weight of silver which has migrated *away* from the anode is $0.0322 - 0.01675 = 0.01545$. Hence the transport no. of Ag is $0.01545 / 0.0322 = 0.479$, and that of NO_3 is $1 - 0.479 = 0.521$.

Absolute velocities of ions.—Let a completely ionised solution of 1 gm. equiv. of electrolyte be electrolysed with a potential gradient of 1 volt per cm. The ions move with speeds of u and v cm. per sec., and since the total charges per gm. equiv. on each kind of ion are $+F$ and $-F$, respectively, the charges transported per sec. are $+uF$ and $-vF$, where $F = 1$ faraday = 96,500 coulombs. Negative charge moving in one direction is equivalent to positive charge moving in the opposite direction, hence the total charge transported per sec. is $uF + vF$, which is the same as the current, viz. $\lambda_\infty = l_c + l_a$. Hence :

$$l_c + l_a = F(u + v) \quad \text{or} \quad l_c = Fu \quad \text{and} \quad l_a = Fv.$$

The units are : l_c and l_a ohm⁻¹ cm.² equiv.⁻¹, and F coulomb equiv.⁻¹ = amp. sec. equiv.⁻¹ = volt ohm⁻¹ sec. equiv.⁻¹. Hence $l_c/F = u$ and $l_a/F = v$ are in (cm. sec.⁻¹) (volt⁻¹ cm.) or cm. per sec. per volt per cm.

Hence the mobilities u and v expressed in cm. per sec. for a potential gradient of 1 volt per cm. can be calculated from the values of l_c and l_a in the table on p. 232. In this way the following values at 18° were found :

H'	0.00326	OH'	0.00181
K'	0.00067	NO ₃ '	0.00064
Ag'	0.00057	I'	0.00069
Na ⁺	0.00045	Cl'	0.00068
NH ₄ '	0.00066	SO ₄ ''	0.00071

Strengths of acids.—Acids in solution owe their acidic properties to the hydrogen ion, and their strengths may be compared by measuring the relative ionisations in solutions containing equivalent weights of the acids in identical volumes. The ionisation is most conveniently determined by the conductivity. Strictly speaking, the degree of ionisation should be calculated from the equation $\alpha = \lambda / \lambda_\infty$, but since the hydrogen ion is much more mobile than any of the anions of acids (as is seen from

the table on p. 232) it carries most of the current, and the equivalent conductivities λ themselves are therefore *approximately* proportional to the ionisations.

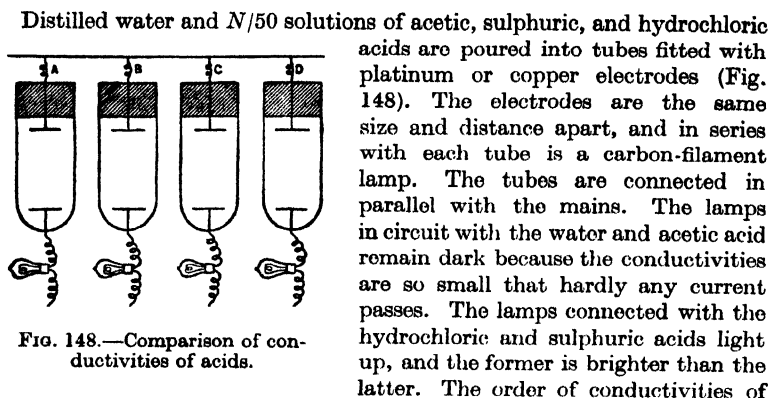


FIG. 148.—Comparison of conductivities of acids.

the three acids : $\text{HCl} > \text{H}_2\text{SO}_4 > \text{CH}_3\text{CO}_2\text{H}$ is also the order of strengths.

The *strength* of an acid is here understood as its degree of ionisation in solution in water, and may not correspond with other less well-defined properties, *e.g.* its corrosiveness or even its power of neutralising peculiar bases such as some organic compounds. The strengths also vary with the solvent.

Another interesting experiment illustrating the varying strengths of acids concerns the *rate of solution of metals* with liberation of hydrogen, an old method later discredited and now again restored (p. 164).

The ionisation of electrolytes.—The purest water which can be obtained is a very poor conductor of electricity. After allowing for the effect of traces of conducting impurities, a slight conductivity due to the ions of the water itself remains. The ionisation of water into hydrogen and hydroxide ions is very small, and a state of equilibrium is set up : $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}'$. To pass a current of 1 ampere through a centimetre cube of pure water at 18° would require a potential gradient of about a million volts, *i.e.* of 500,000 accumulator cells in series. The amount of water ionised is only one gm. mol. in ten million litres (10^{10} ml.)

If 1 gm. mol. of hydrochloric acid is dissolved in water so that the total volume of solution is 1 litre, the conductivity is increased nearly ten millionfold. This is due to the ionisation of the hydrochloric acid : $\text{HCl} = \text{H}^+ + \text{Cl}'$. Nearly all the acid exists in the solution in the form of ions which carry almost all the current.

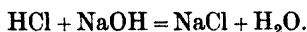
Electrolytes which are largely ionised in solution are called *strong electrolytes*, those which are only slightly ionised are called *weak electrolytes*. The following table gives the *degree of ionisation* α as determined by the conductivity, $\alpha = \lambda/\lambda_\infty$, in $N/10$ solutions ; although the results

for strong electrolytes have been modified by modern theory (p. 310) the general picture given by the table is still significant.

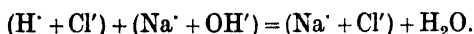
ACIDS		SALTS	
Hydrochloric (H', Cl')	- 0.92	Potassium chloride (K', Cl')	- 0.86
Nitric (H', NO ₃ ')	- 0.92	Sodium chloride (Na', Cl')	- 0.85
Sulphuric (H', HSO ₄ ')	- 0.61	Potassium nitrate (K', NO ₃ ')	- 0.83
Phosphoric (H', H ₂ PO ₄ ')	- 0.28	Silver nitrate (Ag', NO ₃ ')	- 0.82
Hydrofluoric (H', F')	- 0.085	Sodium acetate (Na', CH ₃ COO')	0.80
Acetic (H', CH ₃ COO')	- 0.013	Barium chloride (Ba'', 2Cl')	- 0.75
Carbonic (H', HCO ₃ ')	- 0.0017	Potassium sulphate (2K', SO ₄ '')	0.73
Hydrosulphuric (H', HS')	0.0007	Sodium carbonate (2Na', CO ₃ '')	0.70
Boric (H', H ₂ BO ₃ ')	- 0.0001	Zinc sulphate (Zn'', SO ₄ '')	- 0.40
Cyanoacetic (H', CN')	- 0.0001	Copper sulphate (Cu'', SO ₄ '')	- 0.39
		Mercuric chloride (Hg'', 2Cl')	< 0.01
		Mercuric cyanide (Hg'', 2CN')	very small
BASES			
Sodium hydroxide (Na', OH')	0.91		
Potassium hydroxide (K', OH')	0.91		
Barium hydroxide (Ba'', 2OH')	0.81		
Ammonium hydroxide (NH ₄ ', OH')	0.013		

Neutralisation.—Acids are substances producing the hydrogen ion in solution: $\text{HCl} = \text{H}' + \text{Cl}'$. Bases are substances producing the hydroxide ion in aqueous solution: $\text{NaOH} = \text{Na}' + \text{OH}'$.

When an acid and a base in solution are mixed a salt is formed and the solution becomes neutral. This is usually represented as :



Since the acid, base, and salt are ionised, the reaction occurs between the ions :



The Na' and Cl' the ions of the salt take no part in the change and are free before and after the reaction. Hence *neutralisation is the union of the hydrogen ion of an acid with the hydroxide ion of a base to form practically undissociated water :*



The hydrogen and hydroxide ions have the greatest mobilities, and on neutralisation, when these ions are withdrawn, the conductivity diminishes. This is shown by the following experiment.

Fit a rectangular glass trough with two sheet copper electrodes (Fig. 149). Connect these through an ammeter with two accumulators in series. Pour into the cell N-NaOH solution containing cane sugar to increase its density and coloured with phenolphthalein. Float a slice of cork

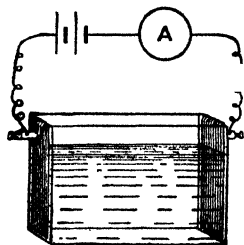


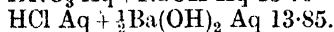
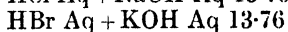
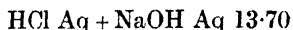
FIG. 149.—Diminution of conductivity on neutralisation.

on this solution, and by means of a burette introduce an equal volume of *N*-HCl as a definite stratum above the alkali. Switch on the current and observe the reading of the ammeter. This is a measure of the current carried by all the ions, Na', H', OH', Cl'. Now stir the two liquids with a glass rod and notice the reduced reading of the ammeter. The ions Na' and Cl' alone now carry the current.

A modification of this method may be used in *titrating* an alkaline or acid solution which is too strongly coloured to allow of an indicator being used.

Heat of neutralisation.—The heat evolved in the neutralisation of one equivalent of a strong base by one equivalent of a strong acid should be the same for different acids and bases, since the reaction in all cases is the union of hydrogen ions from the acid with hydroxide ions from the base to form practically undissociated water: $H' + OH' = H_2O$.

This is verified by experiment; the heat of neutralisation per gm. equivalent of any strong acid and base is equal to about 13.7 k. cal.



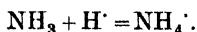
If the acid or the base is weak the un-ionised acid or base will dissociate as neutralisation proceeds, and this dissociation causes an absorption or evolution of heat. An example is the heat of neutralisation of hydrofluoric acid.

This is 16.3 k. cal., and if excess of hydrofluoric acid is added to the neutral fluoride solution 0.3 k. cal. is absorbed. The conductivity of 0.1 *N* hydrofluoric acid shows that only 15 per cent is ionised. On neutralisation, the ionised part of the acid is removed and the unionised part is progressively ionised until all the H' ions are removed and only F' ions remain. It follows from the heat of neutralisation that the ionisation of hydrofluoric acid evolves heat. The heat absorption where excess of acid is added is probably due to the formation of an acid fluoride. If the salt formed is only slightly ionised (a rare case) or is insoluble, the heat of neutralisation will be abnormal, since association of the ions of the salt or the precipitation of the salt, will lead to heat changes.

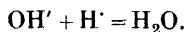
Theory of acids and bases.—In aqueous solutions of acids the hydrogen ion is probably attached to a molecule of water, forming the *hydroxonium ion*, H_3O' : $H' + H_2O = H_3O'$. Regarded as the result of the removal of an electron from a hydrogen atom, the ion H' is the free proton, and this could scarcely be expected to exist in solution to any appreciable extent. The hydrogen ion is probably also *solvated* in other media besides water.

In the theory of acids and bases developed by Arrhenius, the hydroxide ion of bases occupies a position as unique as the hydrogen ion of acids. Another theory, first developed by Lapworth (1908), defines a base as *a substance which unites with hydrogen ion, or an acceptor of protons*, whilst an acid is a donor of protons. All acids have a common function (the formation of hydrogen ions) but this is not

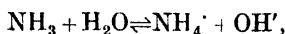
necessary in the case of bases. A neutral ammonia molecule may accept a proton to form the ammonium ion and thus function as a base :



This is just as much a neutralisation reaction as the acceptance of a proton by the hydroxide ion :



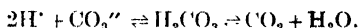
The ammonia molecule may abstract protons from water :



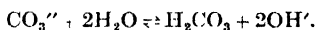
and in this case the greater strength of ammonia as compared with water as a base is shown by the appearance of OH^- ions, *i.e.* by an alkaline reaction.

The acetate ion CH_3COO^- is a strong base, since when a strong acid such as hydrochloric acid is added to solution of sodium acetate the acetate ions unite with practically all the hydrogen ions, forming weakly ionised acetic acid molecules, CH_3COOH .

The anion of any weak acid can function as a strong base. When a strong acid is neutralised with sodium carbonate the reaction is



The weak carbonic acid is unstable and decomposes almost completely. In solutions of sodium carbonate, the CO_3^{2-} ions withdraw hydrogen ions from the water forming very weak carbonic acid and leaving hydroxide ions of the water, which make the solution alkaline :



The real base is the carbonate ion, a powerful hydrogen ion acceptor. This is an example of what is called hydrolysis (p. 302).

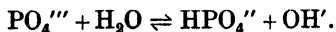
Ionisation in stages.—Molecules which can give more than two ions often dissociate in stages, but not always. Potassium ferrocyanide ionises directly according to the equation: $\text{K}_4\text{Fe}(\text{CN})_6 = 4\text{K}^+ + \text{Fe}(\text{CN})_6^{4-}$, whilst sulphuric acid ionises in two stages: $\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$, followed by $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$. The second stage is incomplete except in very dilute solutions.

At moderate dilutions sulphuric acid should behave as a monobasic acid. The conductivity shows that this is the case. But if the acid is neutralised with a base, the hydrogen ion is completely eliminated with the hydroxide ion of the base to form water: $\text{H}_2\text{SO}_4 + 2\text{OH}^- = \text{SO}_4^{2-} + 2\text{H}_2\text{O}$. As soon as the hydrogen ion corresponding with the first stage of the ionisation: $\text{H}_2\text{SO}_4 = \text{H}^+ + \text{HSO}_4^-$, has been removed the HSO_4^- ion begins to dissociate. The hydrogen ion produced is removed by the base and further ionisation of HSO_4^- goes on until all the HSO_4^- is ionised and only SO_4^{2-} ions are present. This corresponds with the formation of the normal salt and the acid behaves as if it were dibasic.

The later stages of ionisation of polybasic acids are almost always small; *e.g.* with phosphoric acid



the last stage is so slight that the PO_4''' ion in a normal phosphate such as Na_3PO_4 acts as a strong base :



Modern theory of strong electrolytes.—The tendency of modern theory is to assume that strong electrolytes are practically completely ionised and that the change of conductivity with concentration is not due to changes in the number of ions with constant speeds, as in Arrhenius's theory, but to changes of speed of a constant number of ions. In the theory of Debye and Hückel (1923) the electrical forces between the charged ions are assumed to cause each ion to surround itself with an "atmosphere" of ions of opposite charge. When the ion moves it tends to leave this atmosphere behind, and to build up a new one, but owing to the slowness of motion this takes time and there will be an excess of ions of opposite sign behind the moving ion, tending to drag it back. This effect is greater the larger the concentration, hence the ions will move faster in more dilute solutions, and the equivalent conductivity λ will increase on dilution until at infinite dilution, when the ionic forces are negligible, it reaches a constant value λ_∞ .

A second effect retarding the motion of the ions is due to the friction offered by the solvent to the motion of the ions composing the ion atmosphere. This atmosphere must be dragged by the moving ion through the solvent, thus giving rise to a retarding force which also disappears (like the first effect) at infinite dilution, when the frictional force on the central ion alone remains.

The theory shows that the equivalent conductivity λ_∞ , which would be shown if the ions exerted no action on one another, is reduced to the value $\lambda = \lambda_\infty - a\sqrt{c}$, where c = concentration and a is a constant, and Fig. 144 shows that when λ is plotted against the square-root of the concentration it gives, at small concentrations, a straight line. This was discovered empirically by Kohlrausch many years ago. The theory shows that the slope of the λ and \sqrt{c} line should be greater with ions of higher valency (e.g. Cu'' , SO_4'') and this also had been found by Kohlrausch.

Evidence for the theory of electrolytic dissociation.—The main lines of evidence for Arrhenius's theory may be summarised as follows :

- (1) It explains all the facts of electrolysis.
- (2) It explains why the equivalent conductivity of an electrolyte increases with dilution to a fixed maximum limit (λ_∞).
- (3) It accounts for the fact that the properties of electrolyte solutions are additively composed of the properties of the ions.
- (4) It explains reactions in qualitative analysis, e.g. why all chlorides (Cl') give the same reaction with silver nitrate whilst chlorates (ClO_3') do not give this reaction.
- (5) It explains the effect of excess of reagent on the solubility of a precipitate ("solubility product effect", see p. 312), including the "abnormal" cases when complex ions are formed.
- (6) It gives an explanation of "abnormal" osmotic pressures, freezing

point depressions and boiling point elevations shown by electrolytes (see Chapter XVI), and the values of α (extent of ionisation) calculated from the conductivity agree *approximately* with those found by the osmotic methods.

(7) It explains the constant heat of neutralisation of strong acids and bases.

(8) The "anomalies" of strong electrolytes, *e.g.* their deviation from Ostwald's Dilution Law (see p. 299) are explained by an extension of the theory in which ionisation is still assumed.

(9) It explains the action of voltaic cells.

(10) It is in good agreement with theories of the structure of the atom.

All the so-called "objections" to the theory are based on misunderstanding or faulty experiments or interpretations, and need not be stated.

Decomposition potentials.—Although the deposition of a gm. equiv. of any ion requires the passage of the same *quantity* of electricity (96,500 cmb.) the *energy* is different for different ions, and since this is the product of coulombs and volts it follows that the decomposition potentials are different. A Daniell's cell (1.1 volts) will not decompose water whilst an accumulator (2 volts) will do so.

When decomposition proceeds, the electromotive force set up by the products of decomposition deposited on the electrodes acting as a cell must be overcome before further deposition of ions can occur.

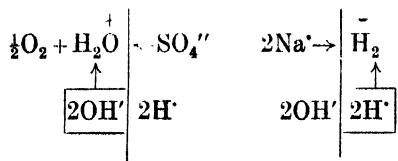
DECOMPOSITION POTENTIALS IN *N*-SOLUTIONS

HNO ₃	1.69	NaOH	1.69	ZnSO ₄	2.35
H ₂ SO ₄	1.67	KOH	1.67	NaNO ₃	2.15
HCl	1.31	AgNO ₃	0.70	NaCl	1.98
HBr	0.94	ZnBr ₂	1.83	CaCl ₂	1.89
HI	0.52				

The table shows that *when only hydrogen and oxygen are deposited*, the decomposition potentials for solutions of salts, acids and alkalis are nearly the same. Le Blanc (1893) assumed that in such cases *the current is carried through the solution by the ions of the salt but the ions of water H' and OH', being more easily deposited and at a lower potential than the metal or acid anions, are deposited at the electrodes forming hydrogen and oxygen gases.* The other ion of water remains in solution at the corresponding electrode, forming acid or alkali with the salt anion or cation which has arrived there after carrying the current through the solution to the electrode.

In the electrolysis of sodium sulphate solution, the sodium and sulphate ions are present in large amounts and carry the current through the solution. At the electrodes these ions are not discharged, since the

hydrogen and hydroxide ions of water are more easily discharged. The result is :



That is, $2\text{NaOH} + \text{H}_2$ are formed at the cathode and $\text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}$ at the anode. The same result was found from the complicated (and probably incorrect) scheme of secondary reactions usually given (see p. 220).

Only very small amounts of hydrogen and hydroxide ions are present in the water but as fast as they are discharged fresh supplies are formed by the ionisation of the water.

In the decomposition of HCl , HBr and HI the potentials are smaller, since halogens and not oxygen are liberated at the anode, and with AgNO_3 silver and not hydrogen is liberated at the cathode.

In the electrolysis of sodium chloride solution (brine) as in the industrial preparation of chlorine and sodium hydroxide (p. 204), the chlorine ions move to the anode, where they are discharged, and the chlorine atoms combine to form chlorine molecules, which appear as chlorine gas : $2\text{Cl}' = \text{Cl}_2 + 2\text{e}$. The sodium ions moving to the cathode are not discharged unless the cathode is of mercury, as in the Castner-Kellner cell. Instead, the hydrogen ions of water discharge and form hydrogen gas as explained above, leaving the hydroxide ions of water to form a solution of sodium hydroxide with the sodium ions round the cathode : $2\text{Na}' + 2\text{H}' + 2\text{OH}' = 2(\text{Na}' + \text{OH}') + \text{H}_2$.

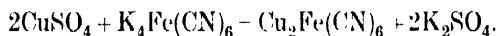
Usually an ion is discharged when the potential difference between the electrode and solution exceeds a certain value called the electrode potential, but in the case of hydrogen ions especially, an overpotential is required (see p. 800). On mercury the overpotential of hydrogen is large, hence sodium ions discharge by preference.

CHAPTER XVI

MOLECULAR WEIGHTS IN SOLUTION

Semipermeable membranes.—When a concentrated solution of copper sulphate in the lower part of a cylinder is covered with a layer of water, the copper sulphate gradually *diffuses* upwards until the solution becomes homogeneous and of uniform colour. The dissolved molecules behave to some extent like a gas; they are in motion and possess kinetic energy. If we could interpose a partition in the solution which would stop the dissolved molecules but would be freely permeable to pure water, we should expect the copper sulphate ions to exert a pressure on the partition. A partition which freely lets through the pure solvent but stops the dissolved substances is called a **semipermeable partition** or (since it is usually prepared in the form of a thin film) a **semipermeable membrane**.

If a drop of copper sulphate solution is introduced from a pipette into a solution of potassium ferrocyanide a skin forms over it, composed of copper ferrocyanide produced as a reddish-brown gelatinous precipitate when the two solutions are mixed :



The pellicle is semipermeable, because no copper salt diffuses through the drop, the ferrocyanide solution remaining clear. The drop expands or shrinks on standing owing to passage of *water* through the pellicle. By holding the drop suspended and with a bright light behind the beaker, the streaks due to changes of concentration may be seen.

An interesting experiment is the "Chemical Garden" first described by Glauber in 1648. A clear solution of sodium silicate of sp. gr. 1.1 made by diluting "water glass" is poured into a tall cylinder and small pieces of ferric, nickel, cobalt, copper and manganous chlorides are dropped in. After a few hours long coloured growths of gelatinous silica coloured by metal hydroxides grow from the crystals. A semipermeable film of silica is formed round each crystal and water enters through this and bursts the film, the salt solution driven out being at once covered by a further film, and so on.

Osmotic pressure.—In order to squeeze pure solvent through a semipermeable membrane a definite pressure must be applied to the solution enclosed in it. At lower pressures no solvent percolates through. The copper ferrocyanide membrane is too weak to support

a pressure, so Pfeffer in 1877 formed it in the wall of an unglazed earthenware porous pot. The semipermeable membrane can be formed in the walls of the pot as follows. The clean and dry pot *B* (Fig. 150) with the glass tube *E* fixed in with sealing wax is gradually lowered into copper sulphate solution whilst the potassium ferrocyanide solution is being poured into the inside. The pot is then placed in a vacuum for some days to draw the air from the pores, and allowed to stand about three weeks in more dilute solutions. It is then attached to the manometer *C* by sealing on the tube *A*, is filled with solution, and placed in water. When the pressure developed reaches a maximum it is read off. This is the *osmotic pressure* of the solution.

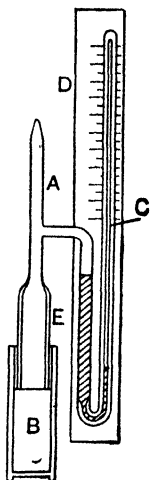


FIG. 150.—Measurement of osmotic pressure.

Morse (1901) prepared the membranes by filling the pot (the pores of which were filled with water) with potassium ferrocyanide solution and immersing it in copper sulphate solution, and then electrolysis with a copper anode outside the pot and a platinum cathode inside. The Cu^{++} and $\text{Fe}(\text{CN})_6^{4-}$ ions moved towards one another in the wall of the pot and formed a film of copper ferrocyanide. As the copper ions move faster, the film is formed near the inner surface of the pot. Morse showed that the membrane was impervious to sugar for 60 days at an osmotic pressure of 12 atm., but allowed water to pass.

Lord Berkeley and Hartley measured the osmotic pressures of concentrated solutions with an apparatus (Fig. 151) in which the porous tube *C*

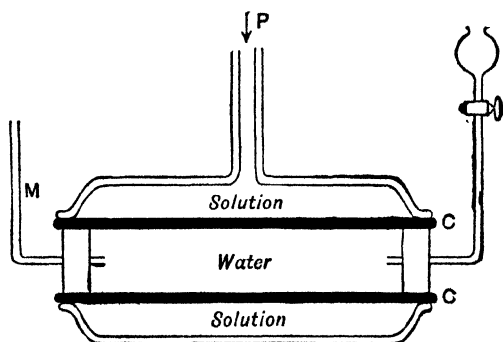


FIG. 151.—Apparatus of Berkeley and Hartley (diagrammatic).

carrying the semipermeable membrane is filled with water and surrounded by the solution to which a pressure *P* is applied to balance the osmotic pressure. The two pressures are equal when no water passes through the membrane, the level in *M* remaining stationary. The membrane is

subjected to equal pressures on both sides and hence is less likely to fail under the high pressures measured. In this method the pressure is applied mechanically to the solution, whilst in Pfeffer's method it is set up by solvent entering the closed pot.

The osmotic pressure of a solution may be defined as the pressure which must be applied to the solution to prevent solvent passing into it through a perfect semipermeable membrane, *i.e.* one which is mechanically rigid and permeable only to the pure solvent. Osmotic pressures are quite large (several atm.) for moderately concentrated solutions, and pressures of 131 atm. have been measured for concentrated solutions.

The laws of osmotic pressure.—The following results were obtained by Pfeffer with dilute solutions of cane sugar :

OSMOTIC PRESSURES OF SUGAR SOLUTIONS AT 0° C.

Concentration C	-	10.03	20.14	40.60	61.38 gm./lit.
Pressure P	-	0.686	1.34	2.75	4.04 atm.
Ratio P/C	-	0.068	0.067	0.068	0.066

The ratio is practically constant, hence *the osmotic pressure at a constant temperature is proportional to the concentration*. Instead of gm./lit. as above, the concentration may be given in gm. mol. per litre. Let V = volume of solution containing 1 gm. mol. of solute (dissolved substance). Then $1/V = C$, $\therefore P/C = PV = \text{const.}$ This is the analogue of Boyle's law.

OSMOTIC PRESSURES OF 1 PER CENT CANE SUGAR SOLUTIONS

Absolute temp. T°	-	273	287.2	305.0
Pressure P (atm.)	-	0.648	0.671	0.716
Ratio $P/T \cdot 10^3$	-	2.37	2.33	2.35

The ratio is practically constant, hence *the osmotic pressure for a given concentration is proportional to the absolute temperature*, or $P = kT$. This is the analogue of Charles's law.

The mean value of P/C at 0° C. is 0.066 ; this is the osmotic pressure in atm. exerted by 1 gram of sugar in 1 litre of solution. Since the molecular weight of sugar is 342, this is also the pressure exerted by 1 gram molecule of sugar in 342 litres. The pressure is inversely proportional to the volume, hence it becomes 1 atm. when the volume containing 1 gram molecule (mol) is $342 \times 0.066 = 22.6$ litres. 1 gm. mol. of ideal gas confined in a space of 22.4 litres at 0° exerts a pressure of 1 atm. The value 22.6 for a molar solution is nearly 22.4, hence solutions obey Avogadro's law.

Van't Hoff in 1885 summarised these results in the statement that dissolved substances obey the gas laws. *The osmotic pressure of a solution is equal to the gas pressure which the solute would exert if all the*

solvent were removed and the dissolved substance were left in the space in the condition of an ideal gas.

This is only approximate but becomes more exact in dilute solutions just as the gas laws are exact only at small pressures.

At 0° a sugar solution containing 1 gm./lit. has an osmotic pressure of 0.066 atm. — $0.066 \times 76 \times 13.6$ gm. per sq. cm. The volume containing 1 mol



J. H. VAN'T HOFF (1852-1911).

is 342,000 ml. The absolute temperature is 273. Hence in the general gas equation (p. 107)

$$PV = RT$$

we have :

$$0.066 \times 76 \times 13.6 \times 342,000 = R \times 273.$$

∴ $R = 85,410$ gm. cm./1°, which is approximately the same as the value for a gas, viz. 84,780.

Osmotic pressures may be used to determine molecular weights in solution, but owing to experimental difficulties the method is rarely used, except for colloids and solutes of high molecular weight, for which parchment paper or collodion membranes can be used.

EXAMPLE.—A solution of 4 gm. of solute in 100 ml. of solution has an osmotic pressure of 5.3 atm. at 15°. Find the molecular weight.

The osmotic pressure at 0°C . is $5.3 \times 273/288$ atm. 1 mol in 22.4 lit. has an osmotic pressure of 1 atm. at 0°C . The actual solution contains 1 gm. in 25 ml. \therefore the mass in 22.4 lit. is $(1/25) \times 22400 = 0.04 \times 22400$ gm. If M is the molecular weight :

$$M : (0.04 \times 22400) = 1 : (5.3 \times 273/288)$$

$$\therefore M = 178.4.$$

Isotonic solutions.—An ingenious method of *comparing* the osmotic pressures of solutions was discovered by de Vries in 1884. He observed under the microscope that the protoplasm content of living plant cells contracts in a concentrated salt solution. This is called **plasmolysis**. The thin outer wall of the protoplasm acts as a **semipermeable membrane** and when the osmotic pressure of the solution outside is greater than that of the natural solution inside the protoplasm, water is forced out of the protoplasm and it shrinks. If the osmotic pressure outside is less than that inside, the protoplasm swells, and when the pressures are equal there is no effect on the cell protoplasm. Hence it is possible to make up a number of solutions all having the **same** osmotic pressure as the cell content, and these solutions must themselves have equal osmotic pressures. These are called **isotonic solutions** and it is found that they contain amounts of dissolved substances in the ratio of the molecular weights when they are non-electrolytes, but in the case of electrolytes the isotonic solutions contain equal numbers of particles (ions + molecules) in equal volumes.

Freezing points of solutions.—Bishop Watson in 1771 and Blagden in 1788 found by experiments with solutions of salts in water that *the lowering of freezing point is proportional to the concentration*. This is usually called “Blagden’s law”. If the depression of freezing point of water by C gm. mols. of cane sugar per 1000 gm. of water is D° , the following experimental results show that D/C is constant :

C	D	D/C
0.000344	0.000645	1.87
0.002303	0.004332	1.88
0.01026	0.01906	1.86
0.01841	0.03434	1.87
0.0365	0.06793	1.86

Raoult in 1883 found experimentally that *if quantities of different substances in the ratio of the molecular weights are dissolved in identical weights of a solvent, the freezing points of the solutions are identical*. A molecular weight in grams of a substance dissolved in 1 kilogram of water depresses the freezing point by 1.858° . This is called the **molecular depression of freezing point Δ** for water. The value of Δ varies from one solvent to another.

Let the depression of freezing point produced by w gm. of solute per kgm. of solvent be D . That produced by the molecular weight M in

1 kgm. is the molecular depression Δ . The two depressions are in the ratio of the concentrations, hence :

$$\frac{D}{\Delta} = \frac{w}{M};$$

$$\therefore M = \frac{w\Delta}{D}.$$

	Δ	M. pt.		Δ	M. pt.
Water -	1.858°	0°	Formic acid	2.8°	8°
Acetic acid	3.9°	17°	Phenol -	7.27°	40°
Benzene -	4.9°	5°	Camphor	40°	180°

Van't Hoff showed that Δ may be calculated from the latent heat of fusion l_f and the absolute melting point T_f of the solvent by the formula :

$$\Delta = \frac{RT_f^2}{1000l_f}.$$

For water : $l_f = 79.74$, $T_f = 273$; also $R = 1.988$ g. cal./1° C.

$$\therefore \Delta = 1.988 \times (273)^2 / (79.74 \times 1000) = 1.858.$$

EXAMPLE.—1.35 gm. of carbon tetrachloride dissolved in 55 gm. of acetic acid depressed the freezing point from 16.750° to 16.132°. Find the molecular weight of carbon tetrachloride.

w = number of gm. of solute per 1000 gm. of solvent = $1.35 \times 1000/55$.

D = observed depression = $16.750 - 16.132 = 0.618^\circ$.

Δ = molecular depression for acetic acid = 3.9° .

$$\text{Molecular weight of solute } M = \frac{w\Delta}{D} = \frac{1.35 \times 1000 \times 3.9}{55 \times 0.618} = 155.$$

The molecular weight calculated from the formula CCl_4 is 153.

Determination of lowering of freezing point.—The apparatus used to find the depression of freezing point is shown in Fig. 152.

A very sensitive **Beckmann Thermometer** D is used, which has a large bulb and only six degrees on the whole scale, the latter being graduated in hundredths of a degree. There is a reservoir at the top of the capillary tube into which mercury can be shaken if higher temperatures are used, or from which mercury can be drawn into the tube and bulb if lower temperatures are used. The actual readings on the scale do not matter, as only their *difference* is required.

About 20 gm. of solvent are weighed into the tube A and a stirrer of bent wire and the thermometer are fitted into the tube through a cork, so that the bulb is covered with liquid. The tube A is fitted through a cork into a large test-tube B , which serves as an air-jacket and prevents too rapid fall in temperature. The tube B is supported in a freezing mixture (*e.g.* ice and salt) contained in the large jar C . The stirrers in the solvent tube and outer jar are worked, and the thermometer observed. The mercury falls steadily to a certain point, when the solvent is slightly supercooled. Freezing then commences and the temperature at once runs up to the freezing point, afterwards remaining stationary. It is then read off with a lens, the thermometer being

gently tapped to prevent any adhesion of mercury to the glass. Suppose the reading is 3.216° (thousandths of the degree are estimated).

The tube *A* is then taken out and allowed to warm till the solvent liquefies. A weighed quantity of the substance is introduced through the side tube and dissolved by working the stirrer. The tube is replaced in the air-jacket and put into the freezing mixture. The process is carried out as with the pure solvent, and the freezing point of the solution read off. Suppose this to be 2.839° ; then *D*, the depression of freezing point, is $3.216 - 2.839 = 0.377^\circ$.

Eutectic mixtures.—When a salt solution freezes only pure ice usually separates and thus the remaining solution becomes more concentrated. Freezing, like distillation, will separate the components of a solution. If the freezing is continued, the solution becomes richer and richer in salt and the freezing point lower and lower, since the more concentrated the solution the lower is the freezing point. This cannot go on indefinitely, because a point is reached when the water left in the solution is only just sufficient to dissolve the salt.

On further cooling, both ice and salt must separate together in the same ratio as they exist in the solution; hence the temperature becomes constant and the whole of the solution solidifies at this eutectic temperature (p. 675).

In Fig. 153, the line from 0° to *E* represents the freezing points of sodium chloride solutions of different concentrations. On freezing, ice deposits until the temperature reaches -21.2° , corresponding with the eutectic point *E*, when ice and solid salt deposit. On cooling a hot saturated solution, solid NaCl separates along *FT*, the curve changing direction at the *transition point T*, when a new solid phase $\text{NaCl}\cdot 2\text{H}_2\text{O}$ appears. This deposits along *TE* until the eutectic point *E* is reached, the solid NaCl previously deposited dissolving and (if present in small quantity) disappearing in the process. If sufficient solid NaCl is present, the solution solidifies completely at *T*. The temperature corresponding with *T* is 0.15° , when the phases present are the two solids NaCl and $\text{NaCl}\cdot 2\text{H}_2\text{O}$, and the saturated solution. The composition of the eutectic

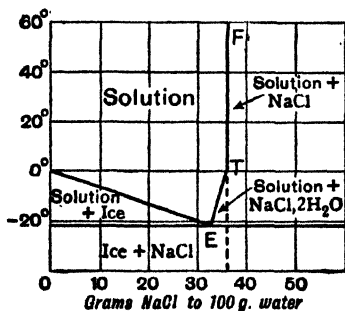


FIG. 153.—System : Sodium chloride—water.

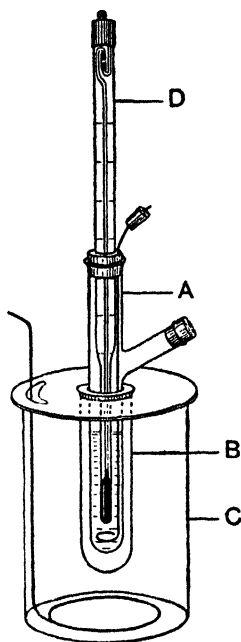


FIG. 152.—Beckmann's freezing point apparatus.

system at E is approximately $\text{NaCl}\cdot 10\text{H}_2\text{O}$, and it was once thought to be a definite "cryohydrate" (p. 70). It is a mixture of crystals of NaCl , $2\text{H}_2\text{O}$ and ice, the only definite hydrate being $\text{NaCl}\cdot 2\text{H}_2\text{O}$. Another eutectic point with anhydrous NaCl and ice is located at $-22\cdot 4^\circ$, but it is very difficult to establish, since the system readily passes into the one involving $\text{NaCl}\cdot 2\text{H}_2\text{O}$ at $-21\cdot 2^\circ$.

More important examples of eutectic points are met with in alloy systems composed of two metals which separate in the pure state on cooling the fused alloy. An example, the lead-antimony system, is described on p. 674.

Vapour pressures of solutions.—If a non-volatile substance is dissolved in a volatile solvent, the vapour pressure of the solution is lower, at a given temperature, than that of the pure solvent. Further, if p_0 is the vapour pressure of the pure solvent, p that of the solution, the ratio $(p_0 - p)/p_0$, or the relative lowering of vapour pressure, is found to be (1) proportional to the concentration of the solution; (2) practically independent of temperature within certain limits; (3) the same for equimolecular amounts of different substances in equal weights of a solvent; (4) the same for different solvents when the ratio of the number of gm. mols. of solute to the total number, solute plus solvent, is the same. (Raoult, 1887).

The molecular lowering of vapour pressure is therefore a constant for a given solvent. In a solution containing N gm. mol. of solvent and n gm. mol. of solute, the relative lowering of vapour pressure is found by experiment to be given by the equation:

$$(p_0 - p)/p_0 = n/(N + n).$$

Thus, if 1 gm. mol. of solute is dissolved in 99 gm. mols. of solvent, there will be a lowering of vapour pressure of 1 per cent, since

$$n/(N + n) = 1/(99 + 1) = 0\cdot 01.$$

The value of N is calculated from the weight of solvent taken divided by its molecular weight in the state of vapour, *i.e.* N is the number of vapour molecules.

EXAMPLE.—Pure benzene, C_6H_6 , has a vapour pressure of 751·86 mm. at 80° . When 2·47 gm. of ethyl benzoate are dissolved in 100 gm. of benzene, the solution has a vapour pressure of 742·6 mm. The molecular weight of benzene vapour is 78; $\therefore N = 100/78 = 1\cdot 282$. Also $(p_0 - p)/p_0 = (751\cdot 86 - 742\cdot 6)/751\cdot 86 = 0\cdot 0123$; $\therefore 0\cdot 0123 = n/(1\cdot 282 + n)$; $\therefore n = 0\cdot 01598$. But $n = 2\cdot 47/(\text{mol. wt. of ethyl benzoate})$; \therefore mol. wt. of dissolved ethyl benzoate $= 2\cdot 47/0\cdot 01598 = 154\cdot 5$. That calculated from the vapour density, or the formula $\text{C}_6\text{H}_5\cdot\text{COO}\cdot\text{C}_2\text{H}_5$, is 150.

Relation between vapour pressure lowering and freezing point depression.—The relation between lowering of vapour pressure and depression of freezing point is shown in Fig. 154. Let OA be the vapour pressure curve of the pure solvent. At the temperature t_0 solvent freezes, and OB is the vapour pressure (sublimation) curve of ice. It has a different slope (much exaggerated in the figure) from OA. The vapour pressure curve of the solution, O'A', lies below that of the solvent, and cuts the ice curve at O',

corresponding with the freezing point of the solution t , where solution and the separated pure ice are in equilibrium, each having the same vapour pressure. If this were not the case distillation would occur between ice and solution and there could not be equilibrium.

Since $O'A'$ lies below OA , O' will lie to the left of O , i.e. $t < t_0$ or the freezing point is lowered as the vapour pressure is lowered. For small depressions OB and $O'O''$ may be regarded as straight lines and OO'' is proportional to $O'O''$, i.e. to $t_0 - t$. The depression of freezing point is proportional to the lowering of vapour pressure.

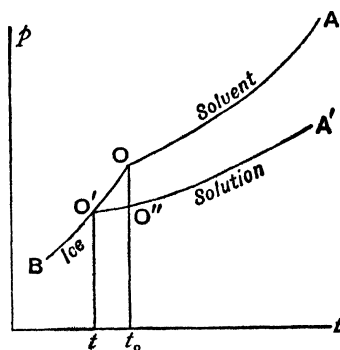


FIG. 154.—Vapour pressure curves of solvent, solution, and ice.

Boiling points of solutions.—Lowering of vapour pressure will cause an elevation of boiling point, since the boiling point is the temperature at which the vapour pressure reaches atmospheric or other total pressure. If salt is dissolved in water the vapour pressure at 100° is less than 760 mm., and it will be necessary to raise the temperature above 100° to reach 760 mm. pressure, i.e. the boiling point of the water is raised by the dissolved substance.

The elevation of boiling point of a solution is often used in the laboratory to produce a heating-bath of higher temperature than 100° . For this purpose, solutions of the very soluble calcium chloride are convenient. They may be boiled in iron vessels. The boiling points for given amounts of anhydrous salt are as follows :

Parts of calcium chloride per 100 parts of water	50	200	325
Boiling point	112°	158°	180°

Such high-temperature baths may replace those using oil, glycerin, or fusible metal, except at temperatures above 200° .

Raoult found that (i) *the elevation of boiling point is proportional to the concentration*, and (ii) *the molecular elevation of boiling point is constant for a given solvent*.

If w gm. of substance in 1 kgm. of solvent raise the boiling point by D° , then if M is the molecular weight of the dissolved substance we have $D/E = w/M$, where E is the molecular elevation of boiling point, i.e. the rise in boiling point for 1 gm. mol. of non-volatile solute in 1 kgm. of solvent. Hence

$$M = \frac{wE}{D}.$$

In some types of apparatus, as in that described below, the molecular elevation is referred to the *volume* of the solution, and in that case E is the elevation produced by 1 gm. mol. in 1 litre of solution at the boiling point. The two values of E are different.

McCoy's apparatus consists of an outer tube *A* containing some of the solvent and an inner tube *B* which is graduated as shown and is fitted with a Beckmann thermometer (Fig. 155).

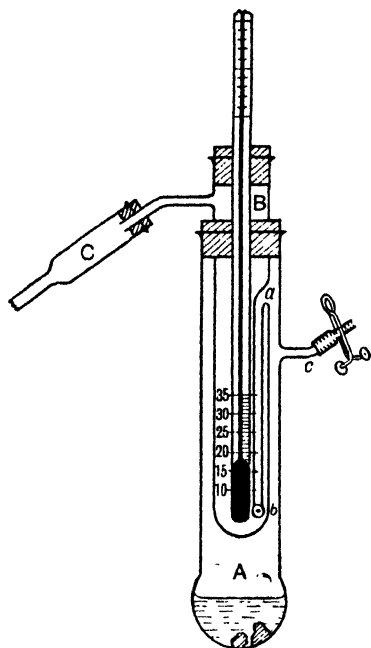


FIG. 155.—McCoy's boiling point apparatus.

About 15 ml. of solvent are put into *B* and the solvent in *A* is boiled, the clip *c* being closed. The vapour from *A* passes into *B* through the inner tube *ab*, which is open to the vapour in *A* at *a* and ends in a perforated bulb at *b*. The vapour condenses and raises the solvent in *B* to the boiling point, a slow distillation taking place through the condenser *C*. The boiling point of the solvent is read off. The clip *c* is now opened (to prevent liquid being drawn back from *B* into *A*) and the boiling stopped. A weighed amount of the substance is now added to *B* by taking out the cork and thermometer, which are then replaced. The clip *c* is closed and the liquid in *A* again boiled. The vapour condenses in the solution in *B* and raises it to the boiling point of the resulting solution. When the temperature is steady the clip *c* is again opened, the thermometer is taken out and the volume of the solution

in *B* is read. The fact that *B* is enclosed in a vapour jacket makes the amount of condensation necessary to raise the solution to its boiling point relatively small.

EXAMPLE.—1.710 gm. of urea gave 28.6 ml. of solution in water, boiling at 100.557°. The molecular elevation is 0.540°. Find the molecular weight.

$$w - 1.710 \times 1000/28.6 = 59.79.$$

$$\text{Observed elevation of boiling point} = 0.557^\circ = D.$$

$$\text{Molecular elevation} = 0.540^\circ = E.$$

$$\therefore M = wE/D = 0.540 \times 59.79/0.557 = 58 \text{ (CON}_2\text{H}_4 = 60).$$

The values of *E* for 1 gm. mol. in 1 kgm. of solvent are given below.

Solvent.	Boiling point °C.	Molecular elevation of boiling point, <i>E</i> .
Water - - -	100	0.52
Methyl alcohol - - -	64.7	0.88
Ethyl alcohol - - -	78.3	1.15
Ether - - -	35.4	2.10
Benzene - - -	80.2	2.57
Chloroform - - -	61.2	3.66

E may be calculated from the latent heat of evaporation of the solvent

l_e , in a similar way to that of Δ from the latent heat of fusion. If T_b is the absolute boiling point,

$$E = \frac{RT_b^2}{1000l_e}$$

It should be noted that the laws of depression of freezing point, elevation of boiling point and lowering of vapour pressure given are true only when the *pure* solvent separates from the solution as solid or vapour, and no solute separates with the ice or distils with the solvent vapour.

Deliquescence.—The lowering of vapour pressure of water by a dissolved substance explains deliquescence, which is the liquefaction of very soluble substances such as calcium chloride, ferric chloride and caustic soda on exposure to moist air. Atmospheric moisture is attracted and a little *saturated* solution is formed. Since this is very concentrated its vapour pressure is less than the partial pressure of water vapour in the atmosphere. The solution goes on absorbing water vapour and since when it is diluted more solid dissolves, in the end all the solid will go into solution.

Electrolytes.—In solutions of electrolytes the osmotic pressure, depression of freezing point and elevation of boiling point are all abnormal. They are all proportional to the total number of solute particles in a given volume, and if the solute is dissociated into ions it produces a larger number of particles, and hence a greater effect for a given mass, than if it were not ionised. A smaller quantity than 1 gm. mol. will thus produce the same effect as 1 gm. mol. of a normal (non-ionised) substance.

If the observed osmotic pressure is P' and the observed depression of freezing point or elevation of boiling point is D' , whilst the normal values are P and D , then the ratio P'/P or D'/D (which are equal to one another) is called *van't Hoff's factor* and denoted by i .

If electrolytes obey the same laws as non-electrolytes, the degree of ionisation could be calculated from van't Hoff's factor $i = \text{observed osmotic pressure} / \text{ideal osmotic pressure}$. Let $\alpha =$ degree of ionisation and let n ions be formed from 1 molecule of electrolyte on complete ionisation. Then in the solution each gm. mol. of dissolved electrolyte gives :

$$(1 - \alpha) \text{ gm. mols. of undissociated electrolyte,} \\ n\alpha \text{ gm. mols. of ions,}$$

or $1 + (n - 1)\alpha$ gm. mols. of solute in all.

$$\text{Hence} \quad \frac{P'}{P} = \frac{D'}{D} = i = \frac{1 + (n - 1)\alpha}{1}$$

$$\therefore \alpha = (i - 1)/(n - 1),$$

from which α can be calculated.

EXAMPLE.—A solution of 4.98 gm. of cadmium iodide in 100 gm. of water freezes at -0.320° . The mol. wt. of CdI_2 is 366; \therefore the solution contains $49.8/366 = 0.136$ mols per 1000 gm. of water. If the salt were undissociated this would produce a freezing point depression of $0.136 \times 1.858^{\circ}$ ($1.858^{\circ} = \text{molar depression}$). The observed depression is 0.320° ,

$$\therefore i = 0.320 / (0.136 \times 1.858) = 1.266.$$

If the dissociation equation is $\text{CdI}_2 = \text{Cd}^{++} + 2\text{I}^{-}$, $n = 3$;

$$\therefore \alpha = (i - 1) / (n - 1) = 0.266 / 2 = 0.133,$$

i.e. 13.3 per cent of the cadmium iodide is ionised.

In the case of strong electrolytes which are largely ionised this method does not give accurate results. Such electrolytes are regarded as practically completely ionised in dilute solutions and the value of α calculated from i has no significance, although i itself still retains its *experimental* meaning.

Relation between osmotic pressure and lowering of vapour pressure.—Van't Hoff in 1885 proved that the osmotic pressure, lowering of vapour pressure, and depression of freezing point of a solution are all closely connected, so that if one is given the others may be calculated without knowing anything beyond the properties of the *pure solvent*.

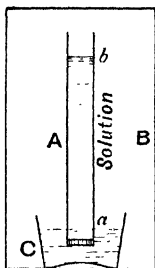


FIG. 156.—Osmotic pressure and vapour pressure.

Let solution be contained in a tube A (Fig. 156), closed at the lower end by a semipermeable membrane in contact with solvent in C. In the tube a column of solution $ab = h$ will be supported by the osmotic pressure. The apparatus is enclosed in a vessel B, which contains only the vapour of the solvent. The vapour pressure is greater at a than at b by the weight of the column ab of vapour. The vapour pressure at a is p_0 , that of the pure solvent in C, whilst the vapour pressure at b is p , that of the solution in A. Hence $p_0 - p$, the lowering of vapour pressure, increases with the height ab , *i.e.* with the osmotic pressure, and for small osmotic pressures will be proportional to the latter, *i.e.* to the concentration of the solution.

The vapour pressure p_0 is greater than that of the solution p by the weight of the column of solvent vapour of height h :

$$\therefore p_0 - p = hd = hpM/RT, \dots\dots\dots(1)$$

where $d = \text{density of vapour} = pM/RT$ where $M = \text{mol. wt. of vapour}$ ($d = M/V$).

The osmotic pressure is:

$$P = hD = RT/V, \dots\dots\dots(2)$$

where $D = \text{density of the dilute solution}$, approximately that of the pure solvent, and $V = \text{vol. of solution containing 1 mol. of solute}$. If the solution contains N mols of solvent and n mols of solute, $V = NM/Dn$; \therefore from (2):

$$hD = RTDn/NM. \dots\dots\dots(3)$$

Substitute h from (3) in (1) ;

$$\therefore p_0 - p = np/N,$$

which by rearrangement gives Raoult's equation, p. 250 :

$$(p_0 - p)/p_0 = n/(N + n).$$

The lowering of vapour pressure has been shown (p. 251) to be proportional to the depression of freezing point, hence the latter is proportional to the osmotic pressure, and therefore to the concentration.

The activity of strong electrolytes.—In the case of electrolytes, the conductivity λ should, according to Arrhenius, give an independent method of finding the degree of ionisation from the formula : $\alpha = \lambda/\lambda_\infty$, whilst the osmotic pressure, boiling point, and freezing point methods should all give a value : $\alpha = (i - 1)/(n - 1)$ (p. 253). If the two values of α agree, this would be a valuable confirmation of the ionisation hypothesis. The following table shows that there is only approximate agreement.

Substance	Concentration gm. mol /litre.	Ionisation from conduc- tivity %.	Ionisation from freezing point %
NaCl - - -	0.001	98.0	98.4
	0.01	93.5	90.5
	0.1	84.1	84.1
K ₂ NO ₄ - - -	0.001	92.3	94.2
	0.005	85.8	88.7
	0.05	70.1	72.6
HCl - - -	0.002	100.0	98.4
	0.01	98.9	95.8
	0.1	93.9	88.6

The newer theory of electrolytes puts a different interpretation on these results, since it assumes that in solutions of the concentrations given in the table the ionisations are practically complete, and hence α has not the meaning attributed to it above. The variations in conductivity are assumed to be due to changes in *mobility* (p. 232) of the ions owing to the electrical forces exerted upon each ion by other ions of opposite sign. The changes in osmotic pressure (and therefore of freezing point) are also regarded as due to the varying attractions exerted between the ions, which at higher concentrations cause the osmotic pressure to have too small a value in the same way as the attractions between gas molecules at higher pressures cause a diminution of pressure on the walls of the vessel.

On the new theory, the osmotic coefficient $(i - 1)/(n - 1)$ and the conductivity ratio λ/λ_∞ are not exactly but only approximately equal. Just as the change in equivalent conductivity is explained by varying mobility of the ions with concentration, so the variations of the osmotic effect are correlated with changes of activity of the ions with concentration, the number of ions remaining the same in both cases.

Let P_i be the osmotic pressure calculated on the assumption that the electrolyte is *completely ionised* and obeys the gas laws, i.e. for a binary electrolyte $P_i = 2cRT$, where $c = 1/V$ is the concentration. On account of

interionic attraction the observed osmotic pressure P is less than P_i , but becomes equal to it at infinite dilution. Let

$$\frac{P_i - P}{P_i} = 1 - g = \theta, \quad (1)$$

where g is the osmotic coefficient, which becomes 1 in very dilute solution, when θ vanishes. Equation (1) holds with D_i and D , or E_i and E , the ideal and observed depressions of freezing point or elevations of boiling point, on the assumption of *complete ionisation*, as well as with P_i and P , since these are proportional.

The value of θ represents the deviation from the ideal gas laws shown by ions in solution. The theory of Debye and Hückel shows that for an electrolyte giving two ions of unit charge ($B^+ + A^-$), at a *total* molar concentration c :

$$\theta = 1 - g = \beta\sqrt{c}. \quad (2)$$

For water at 0° C. as solvent the value of β is 0.372.

It is convenient to introduce an activity coefficient f , defined as

$$f = a/c, \quad (3)$$

a being the activity of the dissolved substance, as explained in Chapter XIX. Then the Debye-Hückel theory leads, for an electrolyte of the type considered, to the relation: $-\log_e f \simeq 1 - f - 3\beta\sqrt{c}$, (4)

where \log_e is the natural logarithm, equal to 2.3026 times the logarithm to the base 10. For water at 25° C. as solvent the value of β is 0.384.

We must remember that λ/λ_∞ , the conductivity ratio, no longer gives the degree of ionisation α , nor does the relation of this to the osmotic pressure etc. take the form previously deduced. Instead we must introduce a new conductivity coefficient:

$$\lambda/\lambda_\infty = f_\lambda. \quad (5)$$

Debye and Hückel's theory shows that, for an electrolyte B^+A^- we have:

$$1 - f_\lambda = K\sqrt{c}, \quad (6)$$

agreeing with experiment in *very dilute solutions* as seen from Fig. 144. It must be kept in mind that (5) and (6), like (1), (2) and (3), imply that the electrolyte is *completely ionised*. Debye and Hückel's theory states further that the constants β and K are independent of the composition of the electrolyte B^+A^- , and depend only on the solvent and the temperature.

The Brownian movement.—An obvious step from the gaseous theory of solution is to identify osmotic pressure with molecular bombardment by the dissolved substance on the semipermeable membrane. Boltzmann showed, on the assumption that the solute molecules have the same mean kinetic energy as gas molecules, that the laws of osmotic pressure follow from the kinetic theory. His calculation dropped out of sight, until it was revived on the basis of researches of Jean Perrin.

If an aqueous suspension of gamboge (a gum-resin familiar to painters in water-colour) is examined under the microscope the par-

ticles are seen to be in motion, each performing little excursions in an apparently erratic manner and moving in a zigzag path. This motion was first observed with suspensions in grains of pollen by the botanist Robert Brown in 1827; it is shown by all suspensions of sufficiently small particles and is known as the Brownian movement.

C. Wiener in 1863 suggested that the cause of the Brownian movement is the unbalanced bombardment of the suspended particles by the molecules of the liquid. This was confirmed by Svedberg in 1906; he found that the length of the path agrees with that calculated from the kinetic theory by Einstein (1905) and Smoluchowski (1906).

Perrin found that in a gamboge suspension there was a gradation in density of distribution of the particles with height (Fig. 157). Near the surface, a rise of $1/20$ mm. halved the number of gamboge particles in unit volume. This is analogous to the fall in density of the atmosphere, but on account of the small weight of the gaseous molecules a height of some hundreds of miles is needed to get the same gradation in density as is found in less than a millimetre with the comparatively massive gamboge particles. The gamboge particles and gaseous molecules are both supported against the action of gravity by their kinetic energies. By counting the numbers of particles it was possible to find the law of distribution at different heights.

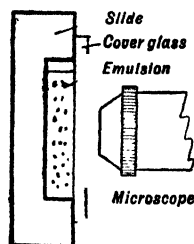


FIG. 157.—Perrin's experiment with gamboge suspension.

If n and n' are the numbers of gamboge particles per cm.^3 at two heights h cm. apart, then if the "solution" obeys the gas laws the osmotic pressures p and p' are in the ratio of n to n' . The ratio p/p' is connected with the height h by the logarithmic barometric pressure formula. The distance h required to produce a given fall of pressure is inversely proportional to the density, or molecular weight, of the gas. To halve the density (or pressure) in an oxygen atmosphere, a vertical ascent of 5 kilometres is required; in hydrogen, with lighter molecules, the ascent is $5 \times 16 = 80$ km., whilst with carbon dioxide, with heavier molecules, it is only $5 \times 16/22 = 3.64$ km. The "molecular weight" of the gamboge particles could thus be calculated from the height in which the number per cm.^3 is halved. The weight of each particle was found by counting the number per cm.^3 , and finding the total weight per cm.^3 . The number of particles N required to make up the molecular weight could thus be found: it was $N = 6.8 \times 10^{23}$, which is nearly the same as the value of Avogadro's number for a gas. By examining the Brownian movement of the suspended particles in tobacco-smoke, de Broglie found $N = 6.43 \times 10^{23}$.

It seems probable that particles in true solutions, much more like those of gases, should also obey the gas laws and that osmotic pressure is caused by molecular bombardment. A partition allowing only water molecules to pass, and arresting gamboge particles, would be subjected to a feeble bombardment and experience a small osmotic pressure. In

the case of true solutions, the number of solute molecules in a given volume is much larger and the pressure is correspondingly greater.

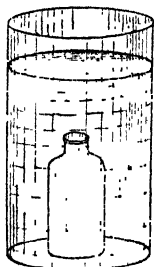


FIG. 158.—Graham's experiment on liquid diffusion.

Liquid diffusion.—Liquid diffusion, mentioned on p. 118 as evidence of molecular motion, was investigated by Graham (1850–62). He placed small bottles containing solutions of various substances in large jars of water (Fig. 158), and determined by analysis the amount of substance diffusing into the water in a given time.

By using apparatus of the same dimensions he obtained comparative results and found that acids and salts diffuse fairly quickly, whereas glue, starch, and albumin diffuse very slowly. The rapidly diffusing substances were (except acids) all crystalline in the solid state, and were called **crystalloids** by Graham. Gum and albumin form amorphous solid masses resembling glue, and were called **colloids** (Greek *kolla*, glue). Graham differentiated between “two worlds of matter, the crystalloid and the colloid,” each with characteristic properties.

Substance.	Times of equal diffusion.	Amounts diffusing in equal times.
Sodium chloride - - -	100	100
Ammonia - - -	160	85
Alcohol - - -	200	47
Glucose - - -	300	36
Gum arabic - - -	700	0.8
Albumin - - -	2100	0.3

Dialysis.—In another set of experiments Graham placed the solution in a shallow bell-jar closed below by a piece of parchment paper or bladder (*i.e.* a solid colloid). This separated the solution from pure water in which the apparatus, called a **dialyser** (Fig. 159), was placed. Crystalloids readily passed through the membrane whereas colloids were either arrested or diffused very slowly.

By means of the dialyser a solution of a colloid may be freed from crystalloidal impurities (*e.g.* salts). A convenient dialyser consists of a parchment paper tube bent into a U-shape, filled with the solution, and placed in a jar through which passes a slow stream of water (Fig. 160). Small “thimbles” of parchment paper, slipped over the end of a glass tube and fixed by a short length of rubber tubing, may also be used. Collodion or cellophane films are more efficient.

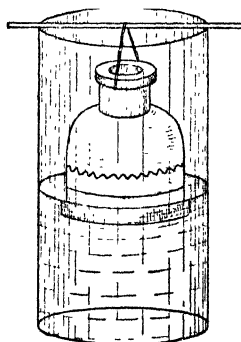


Fig. 159.—Graham's dialyser.

Pour a solution of potassium iodide and starch into a dialyser, consisting of a piece of parchment paper tied tightly over the mouth of a bell-jar.

Suspend the bell-jar with the parchment paper dipping into distilled water in a dish. After half an hour add chlorine water to the water in the dish. A yellow colour, due to liberated iodine, shows that the iodide has diffused through the parchment paper, but the starch is retained, since this would have given a blue colour with the iodine, as may be seen by adding chlorine water to the liquid in the bell-jar.

The distinction between crystalloids and colloids made by Graham is too sharp. Albumin may be obtained crystalline, and common salt may be prepared in colloidal solution by precipitation in liquids (*e.g.* ether) in which it does not form true solutions. The X-ray examination of many colloids, such as colloidal gold with particles 1.86×10^{-7} cm. diameter, colloidal silicic acid, iron oxide, cellulose, etc., shows that they contain very small crystals. The real factor determining whether a substance forms a colloidal solution or a true solution is the size of the dispersed particles; it is more correct to speak of the colloidal state than of "colloidal substances."

Even carefully filtered solutions of cane-sugar show a slight Tyndall effect (p. 3) very much less than that with colloidal solutions. Lord Rayleigh showed that the blue colour of the sky, formerly attributed to scattering of light by dust, can be accounted for by the effect of the gaseous molecules of the atmosphere.

Even carefully filtered solutions of cane-sugar show a slight Tyndall effect (p. 3) very much less than that with colloidal solutions. Lord Rayleigh showed that the blue colour of the sky, formerly attributed to scattering of light by dust, can be accounted for by the effect of the gaseous molecules of the atmosphere.

Classification of colloids.—Although all colloidal materials show more or less common properties, it is usual to separate them into three main groups, although the lines of separation are not always very well defined.

Colloidal solutions are generally called *sols*, and the solid forms, which are frequently gelatinous, are called *gels*. The *sols* are then divided into *suspensoids*, in which the colloid particles are solid, and *emulsoids*, in which they are liquid. There are occasional exceptions to this description and a more recent classification is into *lyophobic* (solvent-repelling) and *lyophilic* (solvent-attracting) colloids, respectively. Lyophobic colloids (*e.g.* arsenious sulphide, ferric oxide, gold) are readily precipitated by electrolytes and have viscosities differing only slightly from that of the solvent; lyophilic colloids (gelatin, albumin) are not easily precipitated by electrolytes and are much more viscous than the solvent. Electrophoresis (p. 7) shows that colloid particles are often *charged*; they are precipitated by ions of opposite charge, the ion being adsorbed. Ions of higher valency (Al^{+++}) are much more effective than those of lower valency (K^+). A positively

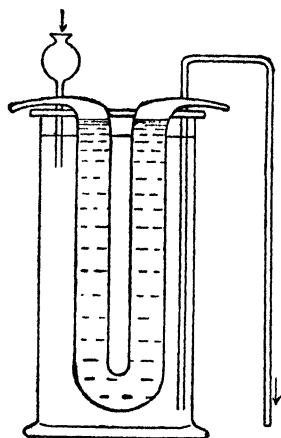


FIG. 160.—Tubular dialyser.

charged sol (ferric oxide) and a negatively charged sol (arsenious sulphide) mutually precipitate each other on mixing.

The distinctions between lyophobic and lyophilic colloids are summarised in the following table.

LYOPHOBIC COLLOIDS	LYOPHILIC COLLOIDS
(i) Non-viscous.	(i) Viscous.
(ii) Not very stable and easily precipitated by electrolytes, the precipitation often being irreversible.	(ii) Fairly stable and not easily precipitated by electrolytes, the precipitation being usually reversible. They "protect" lyophobic colloids from precipitation by electrolytes.
(iii) Non-gelatinising as a rule.	(iii) Gelatinising.
(iv) Particles easily detected by the ultramicroscope.	(iv) Particles not easily detected by the ultramicroscope.
(v) Particles easily show electrophoresis in an electric field.	(v) Particles do not show electrophoresis so markedly.
(vi) Surface tension similar to that of medium (e.g. water).	(vi) Surface tension lower than that of medium, hence solutions easily froth on shaking.

Molecular weights of colloids.—Organic colloids must have high molecular weights; gum arabic, with the empirical formula $C_{12}H_{22}O_{11}$, is acidic, and the small amount of base required for its neutralisation shows that its molecule is much more complex, $(C_{12}H_{22}O_{11})_7$. By the *depression of freezing point* method, high molecular weights have also been found: starch, 25,000; tannin, 1100; silicic acid, 49,000; rubber (in benzene), 6500. The slowness of diffusion and dialysis is understood when one considers that with such enormous molecules (often ultramicroscopically visible) the molecular movement must be very slow, since the square of the velocity is inversely proportional to the molecular weight. The *osmotic pressures* of colloidal solutions are (as would be expected from the large molecular weights), very small but appear to be definite. Pfeffer obtained the following values with 1 per cent aqueous solutions:

	Pressure cm. Hg.	Molecular weight.	
Potassium nitrate	- 178	—	
Cane sugar	- 47	342	
Dextrin	- 16.5	975	
Gum arabic	- 7.2	2230	$[(C_{12}H_{22}O_{11})_7 = 2394]$

Since the molecular weights are inversely proportional to the osmotic pressures (except in the case of potassium nitrate, which is an electrolyte and is abnormal), the figures in the third column may be calculated

from the osmotic pressures and the molecular weight of cane-sugar, 342. Linebarger (1892), using a parchment-paper membrane, found the molecular weight of colloidal tungstic acid by the osmotic method to be 1720, which corresponds with $(\text{H}_2\text{WO}_4)_7 = 1750$.

Graham's suggestion that colloids as a class have *high molecular weights* and *complex molecules*, possibly formed by the association of a number of crystalloid molecules (*e.g.* in the case of tungstic acid), has been generally confirmed.

The molecular weights of colloids have been determined from the *rate of diffusion*, which is inversely proportional to the square-root of the molecular weight. Herzog (1908) found the molecular weight of albumin to be 17,000; Sabanejeff and Alexandroff found 13,000–14,000 by the freezing-point method; Sørensen found 34,000 by the osmotic pressure method, and this value was confirmed by Svedberg, using a centrifugal sedimentation method. Svedberg found 375,000 as the molecular weight of casein. The satisfactory agreement between modern results obtained by different methods seems to indicate that colloids possess definite molecular weights, which may vary with the method of preparation.

CHAPTER XVII

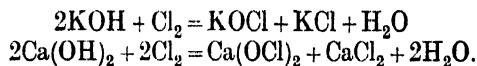
OXIDES AND OXY-ACIDS OF CHLORINE

The known oxides and oxy-acids of chlorine are summarised in the following table :

OXIDES		OXY-ACIDS.
Chlorine monoxide, - - - Cl ₂ O	-----	Hypochlorous acid, HOCl
[Cl ₂ O ₃ unknown] - - -	Chlorous acid, HClO ₂
Chlorine dioxide - - - ClO ₂	. . .	
[Cl ₂ O ₆ unknown] - - - . . .	---	Chloric acid, HClO ₃
Chlorine hexoxide - - - Cl ₂ O ₆	. . .	
Chlorine heptoxide - - - Cl ₂ O ₇	-----	Perchloric acid, HClO ₄

The action of chlorine on alkalis : hypochlorites.—When chlorine is passed into a cold solution of potassium hydroxide so that excess of alkali remains, a liquid smelling rather like chlorine but with a difference is obtained. This liquid, discovered by Berthollet in 1789, is more stable than chlorine water and was used under the name of *eau de Javelle* for bleaching. In England about 1798 the absorption was carried out with milk of lime. Tennant of St. Rollox (Glasgow) in 1799 found that chlorine is absorbed by solid slaked-lime and the resulting *bleaching powder* gave a bleaching liquor with water.

Balard in 1834 showed that these bleaching substances contain salts of hypochlorous acid, HOCl. The reactions give an equimolecular mixture of a hypochlorite and a chloride :

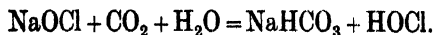


With sodium hydroxide solution a mixture of sodium hypochlorite NaOCl and sodium chloride is formed. This is also produced by adding sodium carbonate to a solution of bleaching powder and filtering from the precipitated calcium carbonate :



or by the electrolysis of brine, so that the chlorine liberated at the anode mixes with the sodium hydroxide produced at the cathode, and the liquid is kept cool.

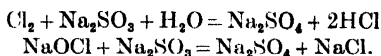
Acids, even carbonic acid (*e.g.* atmospheric carbon dioxide) liberate the very weak hypochlorous acid from its salts ; solutions of hypochlorites smell of the free acid when exposed to air :



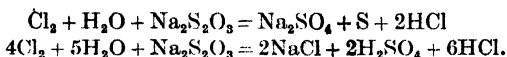
The bleaching action of hypochlorous acid is due to oxidation: $\text{HOCl} = \text{HCl} + \text{O}$. Many colouring matters when oxidised yield colourless or feebly-coloured products. Paper pulp from wood is bleached with sodium hypochlorite solution and acid.

The bleaching action of chlorine water may also be due to the hypochlorous acid it contains, although much free chlorine is present, since the reaction: $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HOCl}$, is reversible. Chlorine does not bleach in the absence of water.

The excess of chlorine, hypochlorous acid or hypochlorite is removed from the bleached material by washing and the last traces by washing with a solution of sodium sulphite or thiosulphate, which acts as an *antichlor* :



The reaction with thiosulphate is complicated :



The equations: $\text{Cl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{O}$, and $\text{HOCl} = \text{HCl} + \text{O}$, show that hypochlorous acid, for the same weight of chlorine, has twice the oxidising activity of free chlorine. There is, therefore, no loss of activity when the chlorine is first absorbed by alkali, although half is converted into inert chloride. It is the available *oxygen* which causes the bleaching action.

If chlorine water is distilled, hypochlorous acid comes over with free chlorine, leaving a solution of hydrochloric acid. The equilibrium: $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{HCl}$, is disturbed by removal of the *volatile* HOCl (or its anhydride, Cl_2O : $2\text{HOCl} \rightleftharpoons \text{Cl}_2\text{O} + \text{H}_2\text{O}$). But if chlorine water is boiled in a flask under a reflux condenser in a stream of chlorine, so that the distillate flows back, it remains unchanged (Richardson, 1903). In *N*/20 chlorine water about 30 per cent, and in *N*/100 about 70 per cent, of the chlorine is hydrolysed into HOCl and HCl.

By cooling to -10° a concentrated solution of sodium hypochlorite, from which sodium chloride has deposited, and shaking, crystals of $\text{NaOCl}, 6\text{H}_2\text{O}$ or $\text{NaOCl}, 7\text{H}_2\text{O}$ separate. These are very deliquescent and melt at 18° ; on cooling, large crystals of $\text{NaOCl}, 5\text{H}_2\text{O}$ are formed.

Calcium hypochlorite is prepared in crystals by passing chlorine into milk of lime and evaporating the clear solution in vacuum. The crystalline hydrate $\text{Ca}(\text{OCl})_2, 4\text{H}_2\text{O}$ is formed. The commercial product (*maxochlor*) is more stable than bleaching powder, is completely soluble in water, and contains about 74 per cent of available chlorine (theoretical hypochlorite oxygen in $\text{Ca}(\text{OCl})_2 = 22.4$ per cent, hence equivalent of $\text{Cl} = 22.4 \times 71/16 = 99.5$ per cent).

Chlorates.—When chlorine is passed into alkali hydroxide solution, hypochlorite and chloride are formed as long as excess of alkali is present, but when excess of chlorine is used the hypochlorite is rapidly converted into chlorate and chloride (Berthollet, 1786). The total reaction is :



but it takes place in stages (see p. 273).

The apparatus is shown in Fig. 161. Chlorine generated from manganese dioxide and hydrochloric acid is washed with a little water, and passed into potassium hydroxide solution (20 gm. of KOH in 40 ml. of water) in the

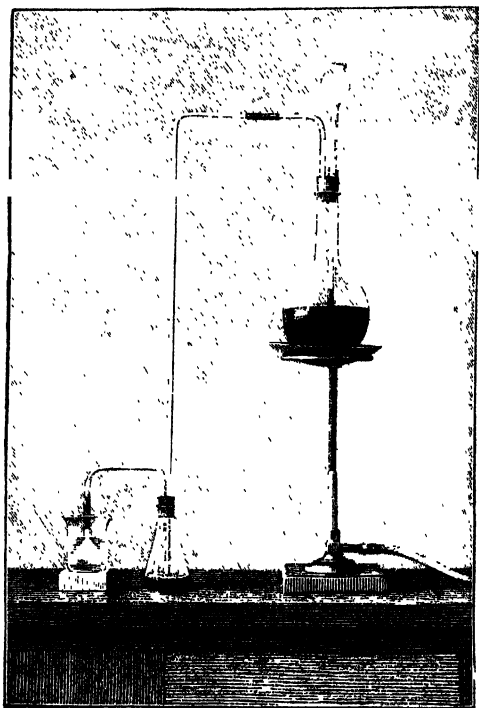


FIG. 161.—Preparation of potassium chlorate.

beaker. Crystals separate, and to prevent the delivery tube becoming choked an inverted funnel is used. When the liquid smells strongly of chlorine it is cooled and decanted from the monoclinic crystals of potassium chlorate KClO_3 which separate (Fig. 162). The crystals are washed once or twice with a little cold water and then recrystallised from hot water. They are sparingly soluble in cold water (8.395 gm. per 100 gm. water at 25°).

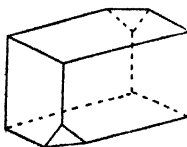


FIG. 162.—Crystal of potassium chlorate.

Potassium chlorate gives certain reactions characteristic of all chlorates :

(1) Solutions give no precipitate with silver nitrate, but on heating the crystals melt and give off oxygen, and the residue when dissolved in water gives a white curdy precipitate of silver chloride with silver nitrate and dilute nitric acid :
 $2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$; $\text{KCl} + \text{AgNO}_3 = \text{AgCl} + \text{KNO}_3$.

(2) If a solution of potassium chlorate is mixed with indigo solution and sulphuric acid and a few drops of sodium sulphite solution are added, the

colour of the indigo is bleached. The chlorate is reduced by the sulphurous acid to a lower oxide of chlorine which has strong bleaching properties.

(3) When concentrated sulphuric acid is added to a little potassium chlorate in a test-tube it turns orange-yellow, and evolves a yellow explosive gas (chlorine dioxide ClO_2) having a peculiar odour: $3\text{KClO}_3 + 2\text{H}_2\text{SO}_4 = \text{KClO}_4 + 2\text{KHSO}_4 + \text{H}_2\text{O} + 2\text{ClO}_2$. On warming there is a crackling noise, due to explosions of the ClO_2 .

(4) Potassium chlorate warmed with concentrated hydrochloric acid gives off a yellow gas (*euchlorine*), which is a mixture of chlorine and chlorine dioxide: $8\text{KClO}_3 + 24\text{HCl} = 8\text{KCl} + 12\text{H}_2\text{O} + 9\text{Cl}_2 + 6\text{ClO}_2$.

Potassium chlorate detonates violently when triturated with phosphorus or sulphur. (*Dangerous*). A little of a mixture of the chlorate and sulphur detonates when wrapped in paper and struck with a hammer.

Perchlorates.—In the decomposition of potassium chlorate by heat, potassium perchlorate KClO_4 is formed: $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}$. This was discovered by Stadion in 1815. The rhombic crystalline form of the perchlorate (Fig. 163) differs from the form of the chlorate. Potassium perchlorate is only sparingly soluble in cold water.

Potassium perchlorate gives the following reactions:

(1) It decomposes at a higher temperature than the chlorate: $\text{KClO}_4 = \text{KCl} + 2\text{O}_2$.

(2) It does not bleach indigo in presence of sulphites.

(3) With concentrated sulphuric acid it does not give a yellow explosive gas, but white fumes of perchloric acid HClO_4 .

(4) It does not react with hydrochloric acid.

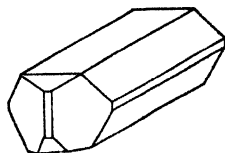
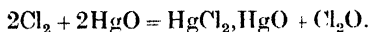


FIG. 163.—Crystal of potassium perchlorate.

Chlorine monoxide.—Chlorine monoxide was discovered by Balard in 1834. It is prepared by passing a slow stream of dry chlorine over yellow precipitated oxide of mercury, previously heated to $300^\circ - 400^\circ$, contained in a cooled tube (Fig. 164). A brown oxychloride of mercury remains and brownish-yellow chlorine monoxide gas passes on:



It is condensed in a freezing mixture to an orange-coloured liquid,

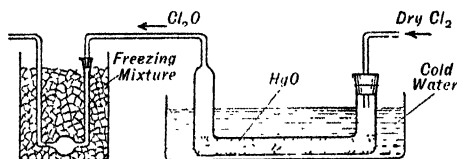


FIG. 164.—Preparation of chlorine monoxide.

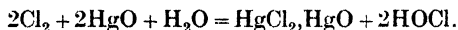
b.pt. 2.0° . The gas may be collected by downward displacement; it attacks mercury (but only slowly) and is soluble in water.

Chlorine monoxide gas explodes readily (although not very violently) on heating, giving a mixture of two volumes of chlorine and one volume

of oxygen: $2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$. The chlorine may be absorbed by sodium hydroxide solution. The volume relations show that one molecule of chlorine monoxide contains one molecule of chlorine Cl_2 , and half of a molecule or one atom of oxygen O, hence the formula is Cl_2O . This is confirmed by the density of the gas.

Liquid chlorine monoxide may explode if the tube containing it is scratched with a file. If free from organic matter, it may be distilled without decomposition. Hydrogen chloride decomposes chlorine monoxide: $\text{Cl}_2\text{O} + 2\text{HCl} = 2\text{Cl}_2 + \text{H}_2\text{O}$. The gas dissolves easily in water to form a golden-yellow solution containing hypochlorous acid: $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HOCl}$. A crystal hydrate $\text{Cl}_2\text{O} \cdot 2\text{H}_2\text{O}$, m.pt. -36° , is formed on strong cooling.

Hypochlorous acid.—This acid is known only in solution. On distillation this decomposes into water and the anhydride of the acid Cl_2O . A solution of the acid is obtained by shaking chlorine water with yellow precipitated mercuric oxide:



The liquid is filtered from the insoluble mercuric oxychloride and is distilled; a dilute solution of hypochlorous acid collects in the receiver.

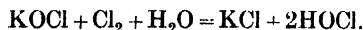
An interesting reaction is the direct oxidation of hydrochloric acid, discovered by Odling in 1860: $\text{HCl} + \text{O} = \text{HOCl}$. A current of air is passed through concentrated hydrochloric acid in a wash-bottle, and then through potassium permanganate solution in a retort heated on a water bath, when hypochlorous acid distils.

Hypochlorous acid is most conveniently prepared from bleaching powder. When dissolved in water, this decomposes into calcium chloride and calcium hypochlorite. To a clear solution of bleaching powder the calculated amount of 5 per cent nitric acid is added slowly from a burette whilst the liquid is kept well stirred; hypochlorous acid is formed: $\text{Ca}(\text{OCl})_2 + 2\text{HNO}_3 = \text{Ca}(\text{NO}_3)_2 + 2\text{HOCl}$. The liquid is distilled and dilute hypochlorous acid is obtained.

Hydrochloric acid reacts with hypochlorous acid with liberation of free chlorine: $\text{HCl} + \text{HOCl} \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$. If an excess of any acid capable of liberating hydrochloric acid from calcium chloride is added to bleaching powder (or its solution) all the chlorine is set free:



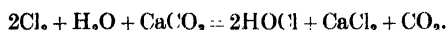
Free hypochlorous acid is formed by the action of chlorine on a hypochlorite solution:



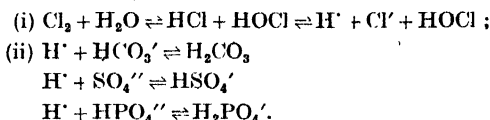
This reaction probably occurs in two stages:

- (a) $\text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons \text{HCl} + \text{HOCl} \rightleftharpoons \text{H}^{\cdot} + \text{Cl}^{\cdot} + \text{HOCl}$.
- (b) $\text{OCl}^{\cdot} + \text{H}^{\cdot} = \text{HOCl}$.

If chlorine is passed into a suspension of calcium carbonate in water, or a solution of sodium bicarbonate, sulphate, or phosphate, hypochlorous acid (not a hypochlorite) is formed :

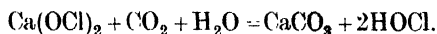


This reaction probably occurs in two stages :

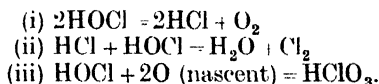


The function of the carbonate, etc., is to remove hydrochloric acid as it is produced, and so prevent reaction (i) coming to a standstill.

Hypochlorous acid is easily made by passing carbon dioxide into bleaching powder solution and then distilling :

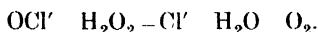


Hypochlorous acid solution is pale golden yellow, colourless when dilute. It is a weak acid, 0.02 per cent ionised in *N*/10 solution, and the salts are hydrolysed in solution : $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}'$. The dilute solution is fairly stable in the dark : concentrated solutions decompose on exposure to light, with evolution of oxygen and chlorine and formation of some chloric acid :



The decomposition is accelerated by platinum black, manganese dioxide, or cobalt oxide. Hypochlorites on heating with cobalt oxide in alkaline solution evolve oxygen : $2\text{NaOCl} = 2\text{NaCl} + \text{O}_2$.

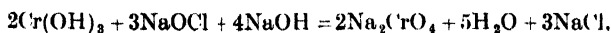
Hypochlorous acid dissolves magnesium with evolution of hydrogen : $\text{Mg} + 2\text{HOCl} = \text{Mg(OCl)}_2 + \text{H}_2$. Iron and aluminium evolve hydrogen and chlorine : copper, nickel, and cobalt evolve chlorine and oxygen. Hypochlorous acid does not precipitate silver nitrate solution. With hydrogen peroxide the acid and its salts evolve oxygen :



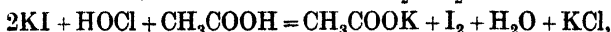
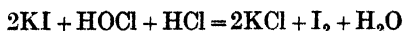
The oxidising properties of hypochlorites : $\text{OCl}^- = (\text{Cl}^- + \text{O})$, are illustrated by the following experiments :

Add sodium hydroxide solution to a solution of manganese sulphate. A white precipitate of manganous hydroxide is formed : $\text{MnSO}_4 + 2\text{NaOH} = \text{Mn(OH)}_2 + \text{Na}_2\text{SO}_4$. Add sodium hypochlorite solution. The precipitate is converted into brown hydrated manganese dioxide : $\text{Mn(OH)}_2 + \text{NaOCl} + \text{H}_2\text{O} = \text{Mn(OH)}_4 + \text{NaCl}$.

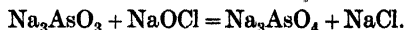
To a solution of chrome alum add excess of NaOCl solution. A yellow solution of sodium chromate $\text{Na}_2(\text{CrO}_4)$ is formed :



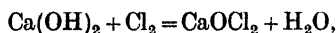
Hypochlorous acid and hypochlorites liberate iodine from potassium iodide (hypochlorites in presence of acetic acid) :



and oxidise sodium arsenite solution to sodium arsenate :



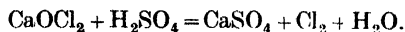
Bleaching powder.—Chlorine gas does not react with *quicklime* at the ordinary temperature, but at a red heat oxygen is evolved and calcium chloride formed : $2\text{CaO} + 2\text{Cl}_2 = 2\text{CaCl}_2 + \text{O}_2$. If chlorine is passed over *slaked lime* it is rapidly absorbed, forming *bleaching powder* or *chloride of lime*. The reaction is usually given as :



most of the water formed remaining in the powder.

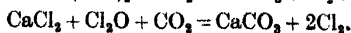
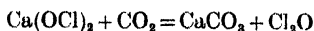
In the manufacture of bleaching powder the slaked lime is spread over the floors of closed lead chambers so as to expose a large surface and somewhat diluted chlorine gas is admitted. At first the chlorine is rapidly absorbed but the reaction afterwards becomes slower. The powder is turned over with wooden rakes and the action continued until absorption is complete, which takes 12–14 hours. In modern works, large rotating inclined iron cylinders cooled externally by water where the reaction is vigorous are used, the slaked lime passing down in the opposite direction to the electrolytic chlorine diluted with air.

Good bleaching powder contains about 35 to 37 per cent of *available chlorine*, i.e. chlorine liberated by acids. Some calcium hydroxide is always present. It should be noted that the *whole* of the chlorine of CaOCl_2 is set free by acid :



Formula of bleaching powder.—Bleaching powder was regarded by Dalton (1813) as a molecular compound of lime and chlorine CaO, Cl_2 , “chloride of lime”. Balard (1835) suggested that it was a *mixture* of equimolecular amounts of calcium hypochlorite and chloride : $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$. This does not agree with the facts : (1) good bleaching powder is not very deliquescent ; (2) alcohol extracts very little calcium chloride from good dry bleaching powder although it readily dissolves calcium chloride ; (3) according to Lunge nearly 90 per cent of the total chlorine of bleaching powder is liberated at 70° by damp carbon dioxide, which has no action on calcium chloride.

Kraut (1882) explained the last reaction by the action of chlorine monoxide on calcium chloride (assumed by Balard to be present) :



The properties of bleaching powder agree with the formula proposed by Odling (1861): $\text{Ca}(\text{OCl})\text{Cl}$, *i.e.* calcium chloro-hypochlorite, which in solution decomposes into calcium chloride and calcium hypochlorite :



Stahlschmidt (1876) proposed the formula $\text{Ca}(\text{OH})(\text{OCl})$.

O'Shea (1883) tested the formulae of Balard, Stahlschmidt and Odling as follows.

He removed any free calcium chloride by treatment with alcohol and determined in the residue : (i) the total lime CaO ; (ii) the total chlorine after decomposition of hypochlorite by ammonia and precipitation as silver chloride ; (iii) the hypochlorite chlorine, liberating iodine from potassium iodide.

The residue after treatment with alcohol, and the above ratios, should be in the different cases :

	Residue	$\frac{\text{CaO}}{\text{total Cl}}$	$\frac{\text{CaO}}{\text{hypochlorite Cl}}$	$\frac{\text{hypochlorite Cl}}{\text{total Cl}}$
1. Balard	$\text{Ca}(\text{OCl})_2$	1 : 2	1 : 2	1 : 1
2. Stahlschmidt	$\text{Ca}(\text{OH})\text{OCl}$	1 : 1	1 : 1	1 : 1
3. Odling	$\text{Ca}(\text{OCl})\text{Cl}$	1 : 2	1 : 1	1 : 2
4. Found	-	1 : 2	1 : 1	1 : 2

Thus, only Odling's formula agrees with the results.

Ditz and Neumann considered that the free calcium hydroxide in bleaching powder is an essential constituent, and that combined water is also present. The active constituent is Odling's compound. Normal bleaching powder is regarded as the compound $3\text{Ca}(\text{OCl})\text{Cl}$, $\text{Ca}(\text{OH})_2$, $5\text{H}_2\text{O}$. In complete absence of moisture a very hygroscopic compound $3\text{Ca}(\text{OCl})\text{Cl}$, $\text{Ca}(\text{OH})_2$, $3\text{H}_2\text{O}$ is formed, whilst at low temperatures $\text{Ca}(\text{OCl})\text{Cl}$, $\text{Ca}(\text{OH})_2$, H_2O can be obtained.

According to Bunn, Clark and Clifford (1935), the first products of the action of chlorine on slaked lime are a basic hypochlorite $\text{Ca}(\text{OCl})_2$, $2\text{Ca}(\text{OH})_2$, and a non-deliqescent basic chloride $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$. On further chlorination, the basic hypochlorite is converted into a mixed crystal consisting mainly of calcium hypochlorite (which forms crystals of $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$), and ordinary bleaching powder is regarded as a mixture of this and the basic chloride.

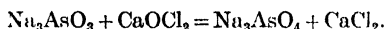
Available chlorine of bleaching powder.—Bleaching powder is mainly used as an oxidising agent, and the active agent is really nascent oxygen. Usually the chlorine equivalent of this active oxygen is returned as available chlorine : $\text{O} (16) = \text{Cl}_2 (71)$. If bleaching powder consisted of $\text{Ca}(\text{OCl})\text{Cl}$, the chlorine equivalent of the active oxygen atom of the hypochlorite radical would be $\text{O} = \text{Cl}_2$, *i.e.* the total chlorine. This would be completely liberated by acids : $\text{CaOCl}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O} + \text{Cl}_2$.

Commercial bleaching powder always contains calcium hydroxide, calcium chloride, and possibly calcium chlorate $\text{Ca}(\text{ClO}_3)_2$, and since the chlorine of the last two is not liberated by acids, and the oxygen of the chlorate is not available for the usual oxidising purposes of

bleaching powder, a distinction is made between the total and available chlorine.

The estimation of the available chlorine of bleaching powder is carried out by one of the following methods :

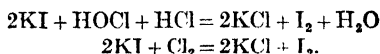
1. Penot's method: A suspension of bleaching powder is titrated with decinormal sodium arsenite solution until a drop of the liquid taken up by a glass rod and put on a piece of filter-paper soaked in potassium iodide and starch solution and dried, no longer gives a blue colour owing to liberation of iodine. The reaction is :



1 ml. of *N*/10 Na_3AsO_3 is equivalent to 0.00355 gm. of available chlorine.

2. Bunsen and Wagner's method : Excess of potassium iodide solution is added to a suspension of bleaching powder and the liquid acidified with acetic acid. Iodine is liberated : $2\text{KI} + \text{HOCl} + \text{CH}_3 \cdot \text{COOH} = \text{CH}_3 \cdot \text{COOK} + \text{I}_2 + \text{H}_2\text{O} + \text{KCl}$. This is titrated with decinormal sodium thio-sulphate solution until the yellow colour has practically vanished : $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6$ (sodium tetrathionate) + 2NaI . A little starch-paste is then added, and the titration continued until the blue colour (due to iodine) vanishes. 1 ml. of *N*/10 $\text{Na}_2\text{S}_2\text{O}_3$ = 0.00355 gm. of available Cl.

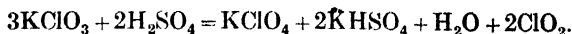
Hypochlorous acid or hypochlorites can be determined in presence of free chlorine by the following reactions :



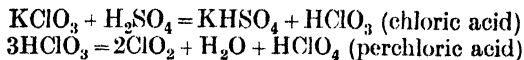
Each molecule of HOCl neutralises one equivalent of acid, whilst chlorine does not affect the acidity. By titrating the iodine and the remaining acid, the amounts of HOCl and Cl_2 may be calculated.

Chlorine dioxide.—Thos. Hoyle in 1797 obtained a yellow explosive gas from potassium chlorate and concentrated sulphuric acid, but he did not recognise it as an oxide of chlorine. The same gas was obtained by Chenevix, but its composition was first determined by Davy in 1815. He showed that it was chlorine dioxide, ClO_2 . On explosion, two volumes of gas gave three volumes of gas consisting of two volumes of oxygen and one volume of chlorine (absorbed by alkali). Hence one molecule of the gas gives one molecule of oxygen O_2 and half a molecule or one atom of chlorine Cl, and the formula is ClO_2 . This is confirmed by the density, which was found by Pebal and Schacherl (1882) to correspond with the formula ClO_2 .

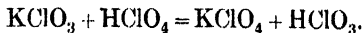
Chlorine dioxide is evolved by the action of concentrated sulphuric acid on potassium chlorate :



The reaction seems to take place in two stages :



the perchloric acid then liberating more chloric acid from the potassium chlorate :

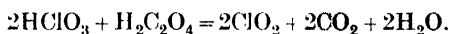


Powdered potassium chlorate is added in small portions to cooled concentrated sulphuric acid in a retort. The orange-yellow paste is very cautiously warmed by placing the retort in lukewarm water and the gas collected by downward displacement, since it is heavier than air, dissolves in water, and attacks mercury slowly, being completely absorbed by it. *There is considerable danger of violent explosion in the preparation of chlorine dioxide and it is recommended that no attempt should be made to prepare it by this method.*

Pure chlorine dioxide is prepared by passing dry chlorine over silver chlorate at 90° and condensing it from the gas in a tube cooled in a freezing mixture (King and Partington, 1926) :



A mixture of chlorine dioxide and carbon dioxide is evolved on heating at 60° a mixture of 40 gm. of potassium chlorate, 150 gm. of oxalic acid crystals, and 20 ml. of water :



When diluted with carbon dioxide the chlorine dioxide is less likely to explode : it can be separated from the gas by condensing it to a liquid by passing into a tube cooled in a freezing mixture. A solution of chlorine dioxide in water is formed by passing the gas into water, when the chlorine dioxide is absorbed, the carbon dioxide mostly passing on.

When chlorine dioxide is passed into a tube cooled in a freezing mixture it condenses to a dark red liquid, b.pt. 11°, freezing at -59° to an orange-red crystalline solid.

The liquid and solid are slowly decomposed by exposure to light. The liquid is violently explosive, but can be distilled without decomposition in absence of organic matter. The gas explodes on heating with a hot wire or glass rod (according to some experimenters at 60°-63°), by an electric spark, and in contact with turpentine, alcohol, or ether.

Add one ml. of cold concentrated sulphuric acid to two portions of 0.5 gm. of potassium chlorate in two test-tubes. A yellow gas with a peculiar smell is formed. Insert a hot glass rod into one tube, into the other throw a small piece of phosphorus. The gas in the first tube explodes; the phosphorus in the second tube inflames spontaneously and explodes the gas. *Care must be used in these experiments, as some acid is usually projected from the tubes.*

Chlorine dioxide (sometimes called chlorine peroxide) is a powerful oxidising agent. This is shown in the following experiments, due to Hoyle and to Fourcroy and Vauquelin.

Equal parts of powdered sugar (or starch) and potassium chlorate are mixed with a spatula on a sand bath, and a drop of concentrated sulphuric acid is allowed to fall on the mixture from a glass rod. The mass ignites and burns violently.

A little potassium chlorate is placed in a glass of water, and one or two small bits of phosphorus are added. If a few ml. of concentrated sulphuric acid are *carefully* poured down a thistle funnel on to the chlorate, ClO_2 is

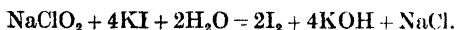
formed. When this comes in contact with the phosphorus it gives a series of flashes of light, accompanied by slight and usually harmless explosions.

Chlorous acid.—Chlorine dioxide dissolves unchanged in water, forming a yellow solution without acid reaction which is stable for several weeks in the dark at 0°. With alkali solutions, however, it forms a mixture of two salts in equivalent amounts, viz. potassium chlorate KClO_3 and potassium chlorite KClO_2 : $2\text{KOH} + 2\text{ClO}_2 = \text{KClO}_3 + \text{KClO}_2 + \text{H}_2\text{O}$. The salts may be separated by evaporation in vacuum over sulphuric acid, when the less soluble chlorate is first deposited.

Pure chlorites are obtained by the action of alkali and hydrogen peroxide on a concentrated solution of chlorine dioxide (see above). The hydrogen peroxide *reduces* chlorine dioxide to chlorous acid: $2\text{ClO}_2 + \text{H}_2\text{O}_2 = 2\text{HClO}_2 + \text{O}_2$. Barium chlorite is formed by passing chlorine dioxide into a suspension of barium peroxide in hydrogen peroxide. Free chlorous acid is obtained in solution by decomposing a solution of barium chlorite with dilute sulphuric acid.

The alkali chlorites have a caustic taste and bleach vegetable colours. They may be distinguished from hypochlorites by the bleaching action *after* addition of sodium arsenite. Silver and lead nitrates precipitate yellow crystalline AgClO_2 and $\text{Pb}(\text{ClO}_2)_2$. These explode on heating; lead chlorite mixed with sugar detonates violently on percussion and has been used for detonators.

Chlorites liberate iodine from iodides:



They react only slowly with arsenious oxide. Chlorous acid gives a violet colour with ferrous sulphate.

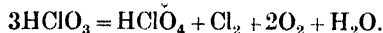
The anhydride Cl_2O_3 of chlorous acid is unknown. The gas prepared by heating a mixture of potassium chlorate and sugar, benzene, or arsenious oxide, with nitric acid, believed to be chlorous anhydride by Millon (1843), was shown by Garzarolli-Thurnlackh (1881) to be a mixture of chlorine dioxide with chlorine. The mixture of chlorine and chlorine dioxide obtained from potassium chlorate and concentrated hydrochloric acid, supposed by Davy to be an oxide of chlorine Cl_2O called *euchlorine* (p. 265), was examined by Pebal in 1875 and the same method was used by Garzarolli-Thurnlackh.

A measured volume of gas was decomposed by heating and the increase in volume determined. The chlorine was absorbed by potash solution and the residual oxygen measured. The volume of oxygen formed was *twice* the increase in volume when the gas was decomposed. This agrees with the formula ClO_2 , since $2\text{ClO}_2 = \text{Cl}_2 + 2\text{O}_2$ (2 volumes give 3 volumes.) It does not agree with the formulae Cl_2O_3 or Cl_2O , as is easily shown.

By passing the "chlorine trioxide" and euchlorine through tubes cooled in a freezing mixture, pure chlorine dioxide was liquefied and chlorine passed on.

Chloric acid.—Chloric acid is formed when hypochlorous acid solution or chlorine water is exposed to light. If a solution of potassium chlorate

is precipitated with hydrofluosilicic acid, sparingly soluble potassium fluosilicate and a solution of chloric acid (which can be filtered) are formed: $2\text{KClO}_3 + \text{H}_2\text{SiF}_6 = \text{K}_2\text{SiF}_6 + 2\text{HClO}_3$. It is more convenient to start with barium chlorate, a solution of which is precipitated with sulphuric acid: $\text{Ba}(\text{ClO}_3)_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HClO}_3$. The excess of sulphuric acid is precipitated with baryta water and the solution is decanted and evaporated in a vacuum desiccator over concentrated sulphuric acid until it contains 40 per cent of HClO_3 . On further concentration the acid decomposes into chlorine, oxygen, and perchloric acid:

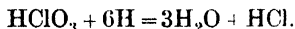


Barium chlorate is made by evaporating a solution of sodium chlorate and barium chloride: $2\text{NaClO}_3 + \text{BaCl}_2 \rightleftharpoons 2\text{NaCl} + \text{Ba}(\text{ClO}_3)_2$. The sodium chloride is deposited, and the hot filtered solution is evaporated, when monoclinic crystals of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ separate. Chloric acid was first prepared (from barium chlorate) by Gay-Lussac in 1814.

Concentrated chloric acid is colourless and fairly stable in the dark. When exposed to light it decomposes and becomes yellow. It has a pungent smell, rather like that of nitric acid, and strong oxidising and bleaching properties. The concentrated acid inflames organic substances such as cotton wool and paper.

Pour a concentrated solution of sodium hydrogen sulphite (NaHSO_3) over crystals of potassium chlorate. A trace of free chloric acid is liberated by the weakly acid NaHSO_3 . The latter is then oxidised by the chloric acid to the strongly acid NaHSO_4 . More chloric acid is liberated, and the velocity of reaction is increased by the action of the products until in one or two minutes the whole mixture foams over, acid sodium sulphate (NaHSO_4) and hydrochloric acid being formed.

Chloric acid evolves some hydrogen with magnesium and zinc, but part of the acid is reduced to hydrochloric acid:



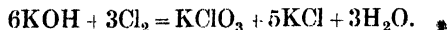
In acid solution, chlorates are reduced to chlorides by iron or aluminium powder, and may be determined in this way. Perchloric acid is not reduced in dilute solution.

The formation of Chlorates.—The preparation of alkali chlorates by passing excess of chlorine into alkali hydroxide solution is described on p. 263.

The student should note that it is not sufficient to say that when chlorine is passed into cold dilute alkali, hypochlorite is formed according to the equation:

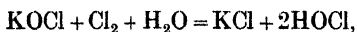


whilst in hot concentrated solution chlorate is formed according to the equation:

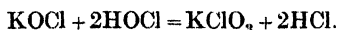


Hypochlorite is always formed first. As soon as the solution contains

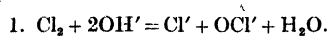
a slight excess of chlorine the hypochlorite is decomposed according to the equation:



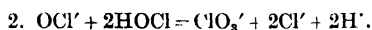
and the free hypochlorous acid oxidises the hypochlorite according to the equation:



The formation of chlorate may, according to Foerster (1899), be represented as follows. As long as the liquid remains alkaline, chloride and hypochlorite are produced:



When the alkali is removed, the hypochlorite ion reacts with the free hypochlorous acid, producing chlorate and chloride ions:



The hypochlorite and hydrogen ions then form hypochlorous acid, and the latter reacts again according to (2):



If equation (1) is multiplied by 3, and equation (3) by 2, then on addition we obtain the usual equation for the total reaction:



Alkaline hypochlorite solutions may be boiled without much decomposition but oxygen is slowly evolved and traces of chlorite are also formed: $2\text{KOCl} = \text{KCl} + \text{KClO}_2$. Hence the equation for the formation of chlorate:

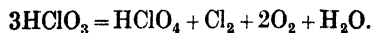


sometimes given, is also incorrect.

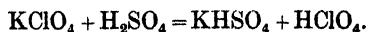
Chlorine hexoxide Cl_2O_6 was first observed by Millon in 1843 as a liquid product of the action of light on chlorine dioxide, but was overlooked until it was rediscovered in 1925 by Bodenstein. It is best obtained by the interaction of ozone and chlorine dioxide at 0° : $\text{ClO}_2 + \text{O}_3 = \text{ClO}_3 + \text{O}_2$. It is a dark red liquid, dens. 1.65, m.pt. 3.5° , less explosive than chlorine dioxide. It dissolves unchanged in water, but with alkali gives a mixture of chlorate and perchlorate: $\text{Cl}_2\text{O}_6 + 2\text{OH}' = \text{ClO}_3' + \text{ClO}_4' + \text{H}_2\text{O}$. The vapour density corresponds with ClO_3 , but the vapour is unstable and the molecular weight in solution in carbon tetrachloride corresponds with Cl_2O_6 .

Perchloric acid.—The most stable oxyacid of chlorine is that containing most oxygen, viz. perchloric acid HClO_4 . Small quantities of very soluble sodium perchlorate NaClO_4 occur in crude sodium nitrate (Chile nitre), and it injures vegetation if the impure nitrate is used as a fertiliser.

Perchloric acid is formed when chloric acid solution is evaporated or distilled:



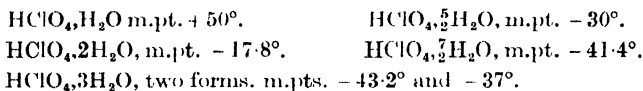
It is usually prepared by distilling potassium perchlorate with concentrated sulphuric acid:



Potassium perchlorate KClO_4 is prepared by heating the *pure* chlorate at 510° in a new porcelain dish, or better at 480° in a silica flask for 8 hours, separating the chloride by cold water, and crystallising the residual perchlorate from hot water: $4\text{KClO}_3 \cdot 3\text{KClO}_4 + \text{KCl}$. Any chlorate remaining may be decomposed by concentrated hydrochloric acid, which does not act on the perchlorate, and the perchlorate purified by recrystallising from hot water.

When potassium perchlorate is distilled with four times its weight of concentrated sulphuric acid in a small retort under atmospheric pressure the perchloric acid collecting in the receiver gradually solidifies to white crystals of the monohydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$, m.pt. 50° . *Anhydrous perchloric acid* was first prepared by Roscoe (1861) by distilling the monohydrate at 110° , but it is more directly obtained by distilling potassium perchlorate with 96-97.5 per cent sulphuric acid under 10-20 mm. pressure at 90° - 160° . It is purified by redistilling at 40° - 60° under 60 mm. pressure.

Anhydrous perchloric acid is a colourless mobile liquid, dens. 1.782 at 15° , boiling with some decomposition at $90'$ under 760 mm. pressure or without decomposition at 19° under 11 mm. pressure. Its m.pt. is -112° . It may explode when heated at atm. pressure. On keeping it becomes dark coloured (perhaps from formation of Cl_2O_6) and in a sealed tube it finally explodes. It is an oxidising agent and inflames paper and wood; when dropped on wood charcoal which has been previously heated and cooled it explodes violently. It fumes strongly in moist air and hisses when dropped into water, owing to the great heat of solution, 20.3 k. cal. per gm. mol. A constant b.pt. solution (72 per cent HClO_4) distils at 203° . The following crystalline hydrates are known:



The crystalline monohydrate $\text{HClO}_4 \cdot \text{H}_2\text{O}$ is apparently *hydroxonium perchlorate* $(\text{H}_3\text{O})\text{ClO}_4$, as its X-ray spectrum is like that of ammonium perchlorate $(\text{NH}_4)\text{ClO}_4$.

The oily aqueous acid is quite stable and is conveniently prepared by adding ammonium perchlorate (a commercial substance) dissolved in concentrated hydrochloric acid to warm concentrated nitric acid in a porcelain dish, and evaporating. The reaction is complicated: $34\text{NH}_4\text{ClO}_4 + 36\text{HNO}_3 + 8\text{HCl} = 34\text{HClO}_4 + 4\text{Cl}_2 + 35\text{N}_2\text{O} + 73\text{H}_2\text{O}$.

The aqueous acid is used in analysis but some care is necessary; it detonates with great violence when evaporated with alcohol, and is probably not so safe as has been stated.

Perchloric acid is a strong acid, as shown by the electrical conducti-

when the temperature of 1 gm. of water is raised 1° C. (p. 178). The *kilogram calorie* (k. cal.) is the corresponding quantity for 1 kgm. of water and 1 k. cal. = 1000 g. cal.

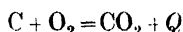
Since heat is a form of *energy*, it can be measured in ergs :

$$1 \text{ g. cal.} = 4.184 \times 10^7 \text{ ergs,}$$

or, as 10⁷ ergs is called a *joule*, 1 g. cal. = 4.184 joules. The *kilojoule* (kj.) or 1000 joules is sometimes used as a unit of heat, and 1 k. cal. = 4.184 kj.

Chemical reactions which evolve heat are called *exothermic*, those which absorb heat *endothermic*. It is standard practice to take heat evolved as positive and heat absorbed as negative, but since evolution of heat corresponds with a decrease of energy the opposite convention is often used. The heat of reaction refers to the case when the products are finally brought to the same temperature, e.g. 18°, as the initial substances.

The heat evolved in the formation of a compound from its elements is equal to the heat absorbed in its decomposition. If the heat evolved is represented by *Q* a *thermochemical equation* such as



means that 12 gm. of solid carbon in a specified form (e.g. graphite) combine with 32 gm. of oxygen gas to form 44 gm. of carbon dioxide, and *Q* g. cal. of heat are evolved, the temperature of the product being finally brought to the temperature of the initial substances, e.g. 18°.

When a reaction takes place at *constant volume* and no work is done by a gas expanding against the pressure of the atmosphere, the heat evolved is the decrease of energy of the system, $-\Delta E$. A compound will contain less or more energy than its elements according as heat is evolved in its formation (*exothermic compound*) or is absorbed (*endothermic compound*). The *energy content* of 1 gm. mol. of a compound is sometimes called the *intrinsic energy* of the compound. The intrinsic energy contents (or energies) of the elements themselves are arbitrarily taken as zero. It is only energy *changes* which can be measured and not the absolute amounts of energy in the elements and in the compound.

$\text{Cu} + \text{S}_{(\text{rhombic})} = \text{CuS} + 11,600 \text{ g. cal.}$ means that 63.5 gm. of copper and 32 gm. of rhombic sulphur have, together, 11,600 g. cal. of energy more than 95.5 gm. of cupric sulphide at the same temperature, and this amount of cupric sulphide has 11,600 g. cal. of energy less than the sum of the energies of the copper and sulphur, this amount of energy being evolved as heat in the reaction.

Heats of reaction.—If E_1 and E_2 are the total energy contents of the initial and final substances in a reaction, the *increase* of energy content due to the reaction is

$$\Delta E = E_2 - E_1 = -Q_v, \dots\dots\dots(1)$$

where Q_v is heat evolved at constant volume. This depends only on the starting materials (defining E_1) and the products (defining E_2), and not on how the reaction is carried out.

If the reaction takes place at *constant pressure* and there is a change in volume, work will be done by the system against the atmospheric pressure if there is an increase in volume, and the heat equivalent of this work will be taken from the heat of reaction. Hence the heat of reaction evolved at constant pressure, or Q_p , will be less than that at constant volume, Q_v , by this amount. If there is a decrease in volume (*e.g.* $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ (gaseous)), then Q_p is greater than Q_v . The difference is significant only when gases take part, as the volume changes of solids and liquids are very small.

If one gm. mol. or mol of a gas of volume V is formed at the constant external pressure P , the work done = (pressure) \times (increase in volume) is PV . Since $PV = RT$ if the change is carried out at the constant temperature T° abs., the external work is RT , or approximately $2T$ g. cal. absorbed (R is nearly 2 g. cal. per 1°).

In a change at constant pressure P the work done is $P(V_2 - V_1)$, and the total heat *absorbed* (in energy units) is

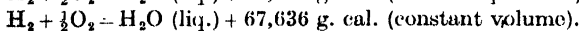
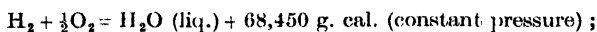
$$\Delta E + P(V_2 - V_1) = (E_2 - E_1) + P(V_2 - V_1).$$

This can be written in the form $(E_2 + PV_2) - (E_1 + PV_1)$, or if we write H for $E + PV$, as $H_2 - H_1 = \Delta H$, the increase in a quantity H , called the *heat content*. If Q_p is the heat of reaction (evolved) at constant pressure,

$$Q_p = -\Delta H. \dots\dots\dots(1a)$$

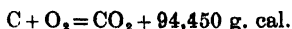
This depends only on the initial and final states (E_1, V_1 and E_2, V_2) at a given constant pressure.

When 2.016 gm. of hydrogen and 16 gm. of oxygen at 0° and 1 atm. pressure, occupying 22.415 + 11.207 = 33.622 litres, are converted into liquid water at 0° , the liquid occupies very nearly 18 ml. The decrease in volume is 33.604 litres, or very nearly 33.600 cm.³ The atmospheric pressure is equal to the pressure of 76 cm. of mercury at 0° , or $76 \times 13.595 \times 980.6$ dynes per cm.²; the work done by the atmospheric pressure, which appears as heat, is $33.600 \times 76 \times 13.595 \times 980.6 = 3.404 \times 10^{10}$ ergs, and since 1 g. cal. is equivalent to 4.184×10^7 ergs, the thermal equivalent of the work is $3.404 \times 10^{10} / 4.184 \times 10^7 = 813.6$ g. cal. Hence the heat of reaction at constant volume is $68,450 - 814 = 67,636$ g. cal. This represents the difference between the chemical energies of the hydrogen and oxygen gases, and that of the liquid water. Thus :

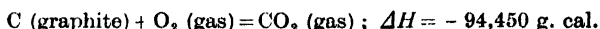


If the reaction occurred at 100°, with production of steam, the heat evolved at constant pressure is diminished by the latent heat of steam, 18×538 g. cal.

With the convention that heat *absorbed* is positive, which is usual in Thermodynamics and is now often used in Thermochemistry, since ΔE and ΔH are the increase of energy and heat content, in the alternative notation the thermochemical equation



(reaction at constant pressure) would be written



The temperature and pressure should also (in strictness) be specified; if they are not, room temperature (18°) and 1 atm. pressure are understood, and there is then no need to specify the physical states, as these are known under these conditions. Symbols are sometimes used to specify the physical states; round brackets (), square brackets [], or no brackets round the symbols mean gases (*e.g.* (H₂O) is steam), solids (*e.g.* [H₂O] is ice) or liquids (*e.g.* H₂O is water). Sometimes the suffixes *g*, *s* and *l* are used for gases, solids and liquids.

Thermochemical quantities can be classified as follows:

(1) **Heat of Combustion**: the heat evolved in the combustion of 1 gm. atom of an element or 1 gm. mol. of a compound in oxygen to give specified products.

(2) **Heat of formation**: the heat change in the formation of 1 gm. mol. of a compound from its elements in specified states.

(3) **Heat of reaction**: the heat change in a reaction with the formula weights in grams.

(4) **Heat of neutralisation**: this is usually given for *equivalent* (not molecular) quantities of acid and base in very dilute solution.

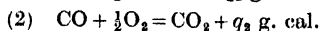
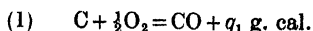
(5) **Heat of solution** for 1 gm. mol. of a compound in a *very large amount of water*, denoted by Aq. (It varies with concentration, but becomes constant for this case; otherwise a heat of dilution is involved when water is added to a solution). *E.g.* NH₃ + Aq. = NH₃Aq. + 8400 g. cal.

In the specification of heat changes, the physical conditions must be stated; *e.g.* whether the substances reacting are solid, liquid or gaseous; whether the reaction is between dry substances or in solution in water, and in the latter case the concentration of the solution must be given; if gases are involved, the temperature and pressure, and whether the reaction is at constant volume or constant pressure, must be stated.

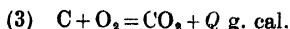
Hess's law.—It is shown above that the heat of reaction, either at constant volume or at constant pressure, depends only on the initial and final states of the reacting substances, and does not depend on the intermediate states. This result was found experimentally by Hess in 1840 and is called *Hess's law*. It is usually stated as follows:

If a reaction is carried out in stages the algebraic sum of the amounts of heat evolved in the separate stages is equal to the total evolution of heat when the reaction occurs directly.

Carbon dioxide may be supposed to be produced from carbon (graphite) and oxygen in two stages :



By adding these equations, according to Hess's law, we find



$$q_1 + q_2 = Q ;$$

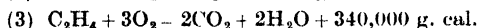
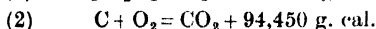
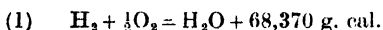
$$\therefore q_1 = Q - q_2 = 94,450 - 67,800 = 26,650 \text{ g. cal.}$$

This enables us to find by calculation q_1 , the heat of reaction (1) which cannot be found directly by experiment.

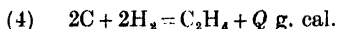
Hess's law shows that a heat of reaction is the algebraic sum of the heats of formation of the products minus the algebraic sum of the heats of formation of the initial substances. For the compounds on the left of the equation may be supposed first decomposed into the elements, and the substances on the right then formed from these elements.

Thermochemical calculations.—Two examples of the use of Hess's law in solving thermochemical problems are given below.

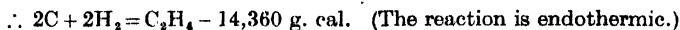
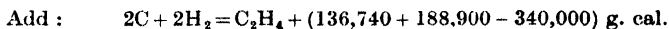
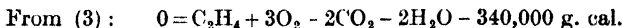
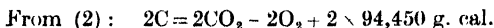
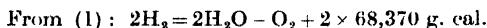
(1) From the following heats of combustion calculate the heat of formation of ethylene C_2H_4 from its elements at constant pressure :



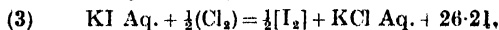
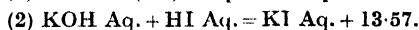
The thermochemical equation to be solved for the unknown Q is :

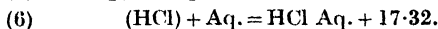
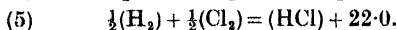


Rearrange equations (1)–(3) so as to give the chemical part of (4) :

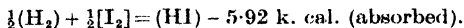


(2) Find the heat of formation of gaseous hydrogen iodide from solid iodine and hydrogen gas from the following heats of reaction, all in k. cal. (for meanings of brackets see p. 280 : Aq. is a large amount of water) :





Write (4), (5) and (6) in the reverse order under (1), (2) and (3) and add. This gives :



The table below gives the heats of formation in k. cal. *evolved* in the formation of 1 gm. mol. at room temperature, the physical states being specified by brackets (see above). Sulphur is rhombic and carbon is graphite.

HEATS OF FORMATION

$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = \text{H}_2\text{O}$	68.37	$2[\text{P}] + \frac{5}{2}(\text{O}_2) = [\text{P}_2\text{O}_5]$	360
$(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$	57.80	$[\text{C}] + (\text{O}_2) = (\text{CO}_2)$	94.45
$(\text{H}_2) + (\text{O}_2) = \text{H}_2\text{O}_2$	45.20	$[\text{C}] + \frac{1}{2}(\text{O}_2) = (\text{CO})$	26.84
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}(\text{Cl}_2) = (\text{HCl})$	22.06	$[\text{C}] + 2[\text{S}] = \text{CS}_2$	- 15.4
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}\text{Br}_2 = (\text{HBr})$	8.65	$[\text{Na}] + \frac{1}{2}(\text{Cl}_2) = [\text{NaCl}]$	98.3
$\frac{1}{2}(\text{H}_2) + \frac{1}{2}[\text{I}_2] = (\text{HI})$	- 5.91	$[\text{Na}] + \frac{1}{2}\text{Br}_2 = [\text{NaBr}]$	86.7
$(\text{H}_2) + [\text{S}] = (\text{H}_2\text{S})$	5.3	$[\text{Na}] + \frac{3}{2}[\text{I}_2] = [\text{NaI}]$	69.3
$\frac{1}{2}(\text{N}_2) + \frac{3}{2}(\text{H}_2) = (\text{NH}_3)$	11.00	$[\text{Ag}] + \frac{1}{2}(\text{Cl}_2) = [\text{AgCl}]$	30.3
$[\text{P}] + \frac{3}{2}(\text{H}_2) = (\text{PH}_3)$	- 5.8	$[\text{Ag}] + \frac{1}{2}\text{Br}_2 = [\text{AgBr}]$	24
$[\text{As}] + \frac{3}{2}(\text{H}_2) = (\text{AsH}_3)$	- 44	$[\text{Ag}] + \frac{1}{2}[\text{I}_2] = [\text{AgI}]$	15
$\frac{1}{2}(\text{N}_2) + \frac{1}{2}(\text{O}_2) = (\text{NO})$	- 21.6	$[\text{Ca}] + (\text{Cl}_2) = [\text{CaCl}_2]$	191
$(\text{N}_2) + \frac{1}{2}(\text{O}_2) = (\text{N}_2\text{O})$	19.7	$[\text{Sr}] + (\text{Cl}_2) = [\text{SrCl}_2]$	198
$[\text{S}] + (\text{O}_2) = (\text{SO}_2)$	71	$[\text{Ba}] + (\text{Cl}_2) = [\text{BaCl}_2]$	205
$[\text{S}] + \frac{3}{2}(\text{O}_2) = (\text{SO}_3)$	93.9	$[\text{Fe}] + \frac{3}{2}(\text{Cl}_2) = [\text{FeCl}_3]$	96.4

Heats of formation from the atoms.—Heats of reaction always refer to the substances taking part in the reaction in the actual states in which they are used. The heat of combustion of carbon in the form of diamond in gaseous oxygen to form carbon dioxide is somewhat different from the heat of combustion of graphite, since these two forms of solid carbon contain different amounts of energy, whereas the same final product is obtained in each case.

If we knew the heat of evaporation of solid carbon, the heat of dissociation of molecular hydrogen into atoms of hydrogen, and the heat of formation of methane from solid carbon and hydrogen gas, we could calculate the heat of formation of gaseous methane from gaseous carbon atoms and gaseous hydrogen atoms. In a similar way, it would be possible to calculate heats of formation of gaseous compounds from the gaseous elements in the atomic state if data for heats of evaporation of the ordinary solid substances, and of dissociation of molecules into atoms, were known.

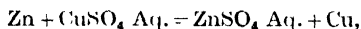
It is possible to calculate (mainly from spectroscopic data) several such heats of dissociation into normal *atoms*, which are given in the following table in k. cal. (*absorbed*) :

H ₂	100.5	NO = N + O	121.4	HF	140
Cl ₂	57	S ₂	102	HCl	101.6
Br ₂	45.2	HD	103.5	HBr	86
I ₂	35.4	D ₂	104.5	HI	66
O ₂	116.4	CO ₂ = C + O	125.8	H ₂ O = H + OH	118
N ₂	170	N ₂ O = NO + N	88.5		

The stability of compounds.—We use the terms stable and unstable to denote whether a given compound is with difficulty resolved into its elements or into related compounds, or whether this change takes place easily and spontaneously.

In general, a substance formed with considerable evolution of energy is stable, whilst a compound formed with considerable absorption of energy is unstable. The stability is roughly proportional to the amount of energy evolved in formation.

Free energy.—Although the heat evolution, or diminution of **total energy**, gives an approximate measure of the stability of a compound, this is really determined by the content of **free energy**. Of the total energy diminution, part is convertible into work by suitable means, the other part appears as heat. The part convertible into work is the free energy. For example, the reaction :



as it occurs in the ordinary way evolves heat, but when it occurs in the Daniell cell part (in this case nearly all) of the energy change is obtainable as electrical energy, which in turn is (theoretically) completely convertible into work. It is this free energy change which gives an accurate measure of the tendency of the system Zn + CuSO₄ Aq. to pass spontaneously into the system Cu + ZnSO₄ Aq., *i.e.* which provides a measure of the relative stability of the two systems. *Only those changes occur spontaneously which lead to a diminution of free energy.* The corresponding statement for **total energy**, that only those reactions occur spontaneously which are attended by evolution of heat, was stated by Thomsen and Berthelot, although the latter had the correct idea in mind when he called it the **principle of maximum work**. This principle is very often approximately true and is a useful guide. The statement is true at the absolute zero, and in many reactions between solids and liquids it holds approximately. The correct statement of the principle is **Nernst's Heat Theorem** (1906) : this allows equilibrium constants to be calculated from heats of reaction.

Free energy values, equilibrium constants, and other thermodynamic quantities can also be calculated by the methods of **statistical mechanics**. In addition to its translational energy, a molecule may have energy associated with the vibration of its atoms (leading to stretching and bending of the valency bonds), and with the rotation of the various parts of the molecule with respect to one another (for example the two CH₃ groups in ethane H₃C·CH₃). A knowledge of the nature of these internal vibrations and rotations, and of the energies involved in them, is required for the calculations, and for relatively simple molecules this knowledge can be obtained by a study of the infra-red and Raman spectra of the substances (p. 439). For most molecules at reasonably low temperatures (say

below 1000°) the possibility of energy changes due to the excitation of the electrons, *i.e.* their transition from one energy level to a higher one (p. 427), can be disregarded. The results of calculations of free energies from spectroscopic data are usually in excellent agreement with values from other sources; any discrepancies between these so-called statistical values and other values (for example, those obtained by an application of the Nernst Heat Theorem) can be attributed to specific peculiarities in the molecules concerned.

CHAPTER XVIII

THE LAW OF MASS ACTION

Chemical affinity.—In the earlier history of chemistry it seems to have been thought that substances closely related to one another (*e.g.* mercury and gold) show the greatest tendency to combine, hence the name **affinity** (from *affinis*, related) was given to the cause of chemical combination.

It was assumed by the alchemists (except Van Helmont) that substances were destroyed on combination, so that an acid and alkali had nothing in common with the salt produced from them. Boyle in his *Sceptical Chymist* (1661), however, remarks that: "gold may be so altered, as to help to constitute several bodies, different from itself, and the other ingredients; yet it may be reduced again into the same yellow, fixed, ponderable, and malleable gold it was, before its mixture with them." Also: "notwithstanding, the particles of some bodies are so closely united, yet there are some which may meet with particles of other denomination, which are disposed to be more closely united with some of them than they are amongst themselves."

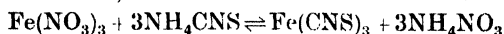
Mayow (1674) said that when ammonia combines with hydrochloric acid the resulting salt (sal ammoniac) shows none of the properties of the acid and alkali. But if sal ammoniac is heated with potash, the ammonia is displaced, "because the acid is capable of entering into closer union" with potash than with ammonia. To show that an acid is not destroyed on neutralisation, he refers to the distillation of nitre with sulphuric acid, which displaces the nitric acid. Nitre on heating does not lose nitric acid, which is kept down by the attraction of the potash, but if sulphuric acid is added the nitric acid comes off, "because the volatile acid . . . has been expelled from the society of the alkaline salt by the more fixed vitriolic acid."

Newton pointed out that potash becomes moist in the air, whilst nitre remains dry, in consequence of an *attraction* for moisture shown by the first substance, but not by the second. Similarly, mercury precipitates silver from its solution in nitric acid, copper in turn precipitates mercury, and iron precipitates copper, because of the increasing attractions of these metals for the acid. He suggested that the attractions might be electrical.

Geoffroy in 1718 and Bergman in 1775 arranged substances in tables, called *affinity tables*, such that a substance standing higher in a column in a table would displace all those standing below it from their compounds. In a series of acids, for example, sulphuric acid displaces hydrochloric acid and nitric acid from their salts, and was supposed to have a greater affinity

is reversible. With increasing mass of potassium carbonate it takes place from left to right; with increasing mass of potassium sulphate it takes place from right to left. After boiling with a given solution of potassium carbonate, an equilibrium is reached with both barium sulphate and carbonate present, and a solution containing both potassium carbonate and potassium sulphate in a definite ratio.

J. H. Gladstone (1855) found that ferric nitrate and ammonium thiocyanate in solution react incompletely to form ferric thiocyanate, which has a red colour, and ammonium nitrate. The reaction:



is reversible. If more ferric nitrate or ammonium thiocyanate solution is added, the red colour deepens, whilst addition of ammonium nitrate favours the reverse reaction and the colour becomes paler.

Prepare two solutions containing 3.5 gm. of crystallised ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 2.3 gm. of NH_4CNS per litre.

Mix 100 ml. of each. A dark-red solution of $\text{Fe}(\text{CNS})_3$ is formed. Add 25 ml. of this solution to 1 litre of water in each of four glass cylinders; a pale brownish-red colour is produced. Keep one jar for reference, and to the other three add: (a) 25 ml. of the ferric nitrate solution; (b) 25 ml. of the thiocyanate solution; (c) 25 ml. of a saturated solution of NH_4NO_3 . Observe the colour change in each case.

Very general statements that *all* reactions are reversible, must be accepted with reserve. Many chemical reactions seem to be irreversible under all known conditions. Magnesium burns in oxygen to form magnesium oxide: $2\text{Mg} + \text{O}_2 = 2\text{MgO}$, and even at the highest temperatures this oxide appears to be stable. The oxidation of mercury in Lavoisier's experiment is a similar reaction but is reversible: $2\text{Hg} + \text{O}_2 \rightleftharpoons 2\text{HgO}$. Again, organic compounds burn in oxygen to produce carbon dioxide and water (if they contain only carbon, hydrogen, and possibly oxygen). Sugar burns in this way: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + 12\text{O}_2 = 12\text{CO}_2 + 11\text{H}_2\text{O}$. There is no trace of sugar left in equilibrium with CO_2 , H_2O , and O_2 , and the reaction is irreversible. Nevertheless, the reverse reaction takes place in green plants under the influence of sunlight.

The law of mass action was first clearly formulated by Guldberg and Waage in 1867. It may be regarded as an experimental fact, but may be deduced: (1) from thermodynamics; (2) from the kinetic theory of gases. A sketch of the second method, due to Guldberg and Waage, is given below.

Kinetic deduction of the law of mass action.—The kinetic theory of gases may be used to deduce the law of mass action for a chemical reaction taking place in a gaseous system. When a mixture of hydrogen and iodine vapour is kept at a fixed temperature, hydrogen iodide is formed; when hydrogen iodide is heated at the same temperature it decomposes into hydrogen and iodine vapour. In both cases the reaction is incomplete and a state of equilibrium is reached.

The same state of equilibrium is reached on heating hydrogen iodide at 444° for a sufficient time as on heating a mixture of hydrogen and iodine vapour, in equivalent proportions, at the same temperature: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

In the reaction between hydrogen and iodine vapour, the probability that a hydrogen molecule will be at a given point is proportional to the number of hydrogen molecules in unit volume. The probability that an iodine molecule will be at the same point is proportional to the number of iodine molecules in unit volume. When the two molecules are at the *same* point a collision results. The number of collisions in unit time is thus proportional to the *product* of the numbers of hydrogen and iodine molecules in unit volume.

Since the number of molecules is proportional to the number of gm. molecules or mols (no. of molecules = no. of mols \times Avogadro's number), the number of collisions in unit volume in unit time is proportional to the product of the number of mols of hydrogen and the number of mols of iodine in unit volume, *i.e.* to the product of the concentrations, $c_{H_2} \times c_{I_2}$. Not every collision results in chemical change, but it is assumed that a constant fraction of the total number of collisions is effective. Hence the rate of reaction of hydrogen and iodine in unit time in unit volume is

$$\text{rate of combination of } H_2 \text{ and } I_2 = k_1 c_{H_2} c_{I_2} \dots \dots \dots (1),$$

where k_1 is a constant at a given temperature, called the *velocity coefficient* for this reaction. Expression (1) gives the velocity of change of hydrogen and iodine into hydrogen iodide.

The hydrogen iodide molecules formed will also enter into collisions and undergo decomposition into hydrogen and iodine molecules. Since two hydrogen iodide molecules must be at the same point for collision, the above reasoning shows that, as the probability of finding *each* at the same point is proportional to the concentration, the probability of finding *two* at the same point is proportional to the square of the concentration. Hence, the velocity of change of hydrogen iodide into hydrogen and iodine is

$$\text{rate of decomposition of HI} = k_2 c_{HI}^2 \dots \dots \dots (2),$$

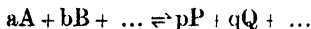
where k_2 is a velocity coefficient for this reaction.

At equilibrium, as many molecules of hydrogen iodide are formed in unit volume in unit time as are decomposed. The velocities (1) and (2) are then equal, and the values of c are now the *equilibrium concentrations*. Hence, for equilibrium :

$$\begin{aligned} k_1 c_{H_2} c_{I_2} &= k_2 c_{HI}^2 \\ c_{HI}^2 / c_{H_2} c_{I_2} &= k_1 / k_2 = \text{const.} = K \dots \dots \dots (3), \end{aligned}$$

where K is called the *equilibrium constant*. This is independent of the concentrations (and hence of the pressure) but depends on the temperature, which changes the direct and reverse reaction velocities by different amounts.

The same reasoning shows that for any reversible reaction :



where a, b, \dots, p, q, \dots are the numbers of reacting molecules of the substances A, B, \dots, P, Q, \dots , the equilibrium constant is :

$$c_P^p c_Q^q \dots / c_A^a c_B^b \dots = K \dots \dots \dots (4)$$

The probability of collision of more than two molecules at the same place is very small, and the kinetic deduction is less suitable for reactions of higher order, but the law of mass action, as (4) is called, may be supposed to follow in the general case from its confirmation by experiment, or it may be deduced from Thermodynamics.

It is usual to write the product of the concentrations of the *products* of a reaction in the numerator of the equilibrium constant, and the product of the concentrations of the reacting substances in the denominator, as above. The larger the value of K , the greater will be the extent of the forward reaction (left to right) when equilibrium is reached. Sometimes the concentrations, in gm. mols. or mols per litre, are denoted by the chemical symbols in square brackets, $[X]$ instead of c_X , and both methods will be used in the sequel.

The equilibrium state.—If follows from the kinetic theory that a state of equilibrium will be the same whether the substances A, B, ... , or the substances P, Q, ... are initially taken. The same equilibrium state is reached on heating hydrogen iodide at 444° for a sufficient time as on heating a mixture of equal volumes of hydrogen and iodine vapour at the same temperature.

This was proved experimentally by Lemoine (1877) and Bodenstein (1894), whose results are shown in Fig. 166. The abscissae are times of heating in minutes and ordinates fractions of HI in the mixture. The upper curve is for the decomposition of HI and the lower for its formation from hydrogen and iodine. Both curves approach the same equilibrium state shown by the horizontal line. The condition for equilibrium is that as much of a substance (*e.g.* HI) is formed in a given interval of time as is decomposed, and equilibrium is a state which is independent of time.

A true chemical equilibrium state is always a balance of two opposite changes, both of which are going on, and is a state of *dynamic* equilibrium and not a static state in which no change at all occurs. This was realised by Williamson in 1850.

Homogeneous and heterogeneous equilibria.—Equilibrium states are divided into (i) *homogeneous equilibria* in which the whole system forms only one phase, or is wholly in the same physical state (usually gas or liquid), as with the hydrogen and iodine system; and (ii) *heterogeneous equilibria* when more than one phase is present. Examples of heterogeneous equilibria are those of liquid with vapour, and solid with liquid, in physical changes, and the decomposition of barium peroxide by heat

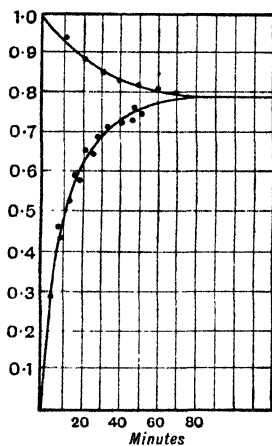


FIG. 166.—Attainment of equilibrium state.

as a chemical change : $2\text{BaO}_2 \rightleftharpoons 2\text{BaO} + \text{O}_2$. In this case oxygen molecules re-form barium peroxide by collision with baryta (BaO).

The rate of decomposition of BaO_2 is constant at a given temperature, and when the rate at which BaO_2 is formed from BaO and O_2 is equal to the rate at which it decomposes, equilibrium is reached. The rate of formation of BaO_2 is proportional to the number of collisions of oxygen molecules per second, and this to the pressure of the oxygen gas ; hence equilibrium is reached with a definite pressure of oxygen. At higher pressures, oxygen is absorbed to form barium peroxide ; at lower pressures barium peroxide decomposes into baryta and oxygen. The equilibrium pressure does not depend on the amounts of the solids (BaO and BaO_2) present.

It might be thought that a greater surface of BaO would offer more opportunities for oxygen molecules to recombine, and hence lead to a lower oxygen pressure. Ostwald pointed out that the equilibrium is reached in the *surface of separation* of the solids. The oxygen is at first absorbed by barium oxide to form a layer of barium peroxide, and barium peroxide in decomposing forms a layer of barium oxide. The solids just below the surface of separation come into equilibrium with it by loss or gain of oxygen molecules, and equilibrium is reached when as many oxygen molecules enter as leave the interface in the same time. The same reasoning applies to the decomposition of calcium carbonate : $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$.

Effect of volatility or insolubility.—Berthollet pointed out that a reversible reaction may go to completion when a product is removed from the sphere of action by its volatility (when it passes away as a gas) or by its insolubility (when it deposits as a solid). In both cases the substance ceases to exert an influence on the equilibrium state.

If calcium carbonate is heated in a closed vessel an equilibrium state is reached owing to the reversibility of the reaction : $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. As many molecules of carbon dioxide are formed by decomposition in a given time as are absorbed by combination with the calcium oxide. But if the heated calcium carbonate is exposed to the atmosphere, or is in a current of air, the carbon dioxide is carried away and cannot recombine with the calcium oxide. The calcium carbonate may then decompose completely into calcium oxide and carbon dioxide.

When iron is heated in steam in a closed vessel, oxide of iron and hydrogen are formed : $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$. Since in the same conditions oxide of iron is reduced by hydrogen a state of equilibrium is reached : $3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$, and this is the same whether iron is heated in steam or iron oxide is heated in hydrogen. If a current of steam is passed over heated iron, the hydrogen formed is removed with the excess of steam and the iron may be completely oxidised. If a current of hydrogen is passed over heated iron oxide, the steam formed is carried away by the excess of hydrogen and the oxide may be completely reduced.

The effect of *volatility* was pointed out by Mayow in 1674 (p. 285) for the equilibrium : $\text{KNO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{KHSO}_4 + \text{HNO}_3$, which is disturbed by the removal of the volatile nitric acid. The reverse reaction

was proved by Baumé in 1773 by crystallising out potassium nitrate from a solution of potassium sulphate in concentrated nitric acid.

The effect of *insolubility* appears when a reaction product is precipitated from the system and ceases to have an effect on the equilibrium. In the reaction $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{BaSO}_4 + 2\text{HCl}$, the barium sulphate precipitates and the reaction goes practically to completion since the concentration of BaSO_4 in the solution is very small. Precipitated barium sulphate is appreciably soluble in boiling concentrated hydrochloric acid.

Investigation of equilibrium states.—Since states of equilibrium are disturbed when one or more of the reacting substances are removed from the sphere of action, and also by a change of temperature, it is often difficult to find the true equilibrium state which is reached at a higher temperature when the system is cooled to atmospheric temperature for analysis. Use is made of the fact that *the velocity of reaction is much smaller at lower temperatures*, so that if the system is cooled very rapidly the equilibrium is (as it were) “frozen”, and the composition of the resulting system may be the same as that of the equilibrium state at the higher temperature.

If hydrogen iodide is heated at 444° till equilibrium is reached, and the bulb containing the equilibrium mixture of gases: $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ is rapidly cooled, solid iodine deposits and a gaseous mixture of hydrogen and hydrogen iodide remains. By opening over potassium iodide solution the iodine and hydrogen iodide dissolve and the hydrogen remains. The iodine may be titrated and the volume of hydrogen measured, and so the amounts of HI, H_2 and I_2 in the equilibrium mixture at 444° can be found. This method was used by Bodenstein (1894).

In the dissociation of steam: $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$, the reaction velocity at the high temperature is so large that very rapid cooling is necessary to freeze the equilibrium state. Grove (1847) heated a platinum wire electrically in steam. The products of dissociation formed on the surface of the wire passed into the diluting and cooling atmosphere of steam, and their recombination was prevented. After a long time the gas mixture, which continually came in contact with the hot wire, reached equilibrium at the temperature of the wire.

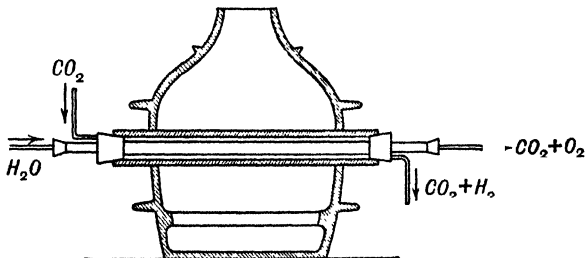


FIG. 167.—Deville's experiment on dissociation.

Deville (1864) used the apparatus shown in Fig. 167. A wide glazed porcelain tube had an unglazed porcelain tube inside it, and the tubes were strongly heated. Steam was passed through the inner tube and

carbon dioxide through the space between the tubes. The gases from both tubes were collected over potassium hydroxide solution, which absorbs carbon dioxide. The hydrogen and oxygen formed by dissociation of the steam were partly separated by more rapid diffusion of the hydrogen through the porous inner tube, most of the oxygen remaining. The gas from both tubes was collected in the same receiver and 1 c.c. of detonating gas ($2\text{H}_2 + \text{O}_2$) was collected for every gram of steam passed through.

Deville passed carbon dioxide rapidly through a glazed porcelain tube packed with bits of porcelain and heated at 1200° to 1300° . The gas was collected over potassium hydroxide solution and a small volume of a mixture of carbon monoxide and oxygen was obtained: $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$. In other experiments, Deville passed a gas through a heated porcelain tube with a narrow axial silver tube cooled by flowing water, which chilled the gas mixture so that some of the products of dissociation were obtained. These experiments are usually described as the "cold-hot tube method."

The following table gives the percentage dissociation of steam as found by Nernst and von Wartenberg (1906). They passed steam mixed with some detonating gas ($2\text{H}_2 + \text{O}_2$) through a strongly heated porcelain tube and collected the detonating gas, chilled by passing through a porcelain capillary tube, over mercury, the volume of liquid water condensed being also measured. Grove's heated wire method was used by Langmuir (1906) and Holt (1907).

T° abs.	10 atm	1 atm.	0.1 atm	0.01 atm
1000	- 1.39×10^{-5}	3.00×10^{-9}	6.46×10^{-5}	1.39×10^{-4}
1500	- 1.03×10^{-2}	2.21×10^{-2}	4.76×10^{-2}	0.103
2000	- 0.273	0.588	1.26	2.70
2500	- 1.98	3.98	8.16	16.6

At the melting point of platinum (1755°) and 760 mm. pressure, about 6 molecules of steam in every thousand are dissociated. At 7.6 mm. pressure this increases to 27.

Equilibrium calculations.—The following examples illustrate the quantitative application of the law of mass action. (For further examples, see J. R. Partington and K. Stratton, *Intermediate Chemical Calculations*, Macmillan, Chapter X).

EXAMPLE 1.—7.94 c.c. of hydrogen (measured at S.T.P.) and 0.0601 gm. of solid iodine were heated in a sealed bulb at 444° till equilibrium was reached. 9.52 c.c. of hydrogen iodide (measured at S.T.P.) were formed.

At S.T.P. 2×127 gm., i.e. 2 gm. mols., of iodine vapour would occupy 22.42 lit. or 22420 c.c., hence the volume of iodine vapour initially present was $22420 \times 0.0601/2 \times 127 = 5.30$ c.c.

The 9.52 c.c. of hydrogen iodide were formed from 4.76 c.c. of hydrogen and 4.76 c.c. of iodine vapour, hence in the equilibrium mixture:

$$\begin{aligned} \text{vol. of hydrogen} &= 7.94 - 4.76 = 3.18 \text{ c.c.} \\ \text{vol. of iodine vapour} &= 5.30 - 4.76 = 0.54 \text{ c.c.} \\ \text{vol. of hydrogen iodide} &= 9.52 \text{ c.c.} \end{aligned}$$

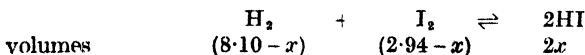
If V lit. is the volume of the bulb, the concentrations in gm. mol./lit. are : $[H_2] = 3.18/22420V$, $[I_2] = 0.54/22420V$, $[HI] = 0.52/22420V$, since 1 gm. mol. of gas at S.T.P. occupies 22420 c.c.

The value of the equilibrium constant at 444° is thus :

$$K = [H_2] \times [I_2] / [HI]^2 = 3.18 \times 0.54 / (0.52)^2 = 0.01895,$$

the factor $22420V$ cancelling. This shows that the equilibrium composition in this case is independent of the volume.

Now suppose that 8.10 c.c. of hydrogen and 2.94 c.c. of iodine vapour (both reduced to S.T.P.) are heated together at 444° . What volume of HI is formed at equilibrium ? Let $2x$ c.c. be formed. Then :



$$\therefore (8.10 - x)(2.94 - x) / 4x^2 \quad K = 0.01895.$$

The solution of the quadratic equation gives $x = 2.825$ or 9.12 . Only the root 2.825 is possible, since 2.94 c.c. of iodine vapour can give only 5.88 c.c. of HI as a maximum. Hence the volume of HI formed is $2 \times 2.825 = 5.65$ c.c. Bodenstein by experiment found 5.66 c.c.

EXAMPLE 2. 2.0 gm. of phosphorus pentachloride sealed in a vacuous bulb of 200 c.c. capacity were heated at 200° . If PCl_5 is 48.5 per cent dissociated at 200° at 1 atm. pressure, find the pressure developed in the bulb.

2.0 gm. $PCl_5 = 2.0/208 = 0.0096$ gm. mol. (mol. wt. of $PCl_5 = 208$). Let x be the degree of dissociation of the PCl_5 under the conditions of the experiment, the volume V being 0.2 lit. The concentrations are :

$$[PCl_5] = 0.0096(1 - x) / 0.2, [PCl_3] = [Cl_2] = 0.0096x / 0.2.$$

The equilibrium constant is $K = 0.0096x^2 / 0.2(1 - x)$(i)

At 200° at 1 atm. pressure the PCl_5 is 48.5 per cent dissociated. But 1 mol of PCl_5 forms $(1 - x)$ mols of PCl_5 and x mols each of PCl_3 and Cl_2 , or $(1 - x) + 2x = 1 + x$ mols in all. At S.T.P. the mixture occupies $(1 + x) \times 22.4$ lit., and at 200° , $22.4 \times 1.485 = 473/273 = 57.6$ lit.

The equilibrium constant is $K = [PCl_3][Cl_2] / [PCl_5]$.

$$[PCl_3] = 0.485/57.6, [Cl_2] = 0.485/57.6, [PCl_5] = (1 - 0.485)/57.6 = 0.515/57.6,$$

$$\therefore K = (0.485)^2 / 0.515 \times 57.6 = 0.00793. \dots\dots\dots(ii)$$

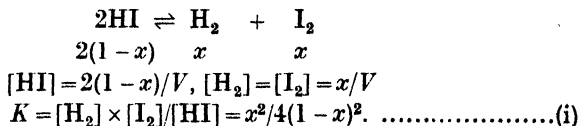
It should be noted that this expression, unlike the one for hydrogen iodide, includes the volume, hence the equilibrium composition (but not K) depends on the volume. From the two expressions (i) and (ii) it is found that the significant root is $x = 0.332$.

The number of mols in 200 c.c. is thus 1.332×0.0096 and the pressure will be

$$1.332 \times 0.0096 \times \frac{22.4}{0.2} \times \frac{473}{273} = 2.48 \text{ atm.}$$

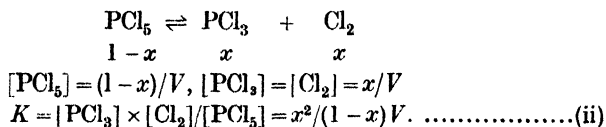
Effect of pressure on equilibrium composition.—It must be emphasised that the equilibrium constant K does not depend on pressure but only on temperature, whereas the composition of the equilibrium mixture (specified by the value of x in the above examples) may depend on the

volume or pressure. When the reaction does not lead to a change of volume, a pressure change has no effect on the equilibrium composition. This is the case with the dissociation (or formation) of hydrogen iodide :



Since this expression is independent of volume, change of volume or of pressure will have no influence on x . The same result applies to the case $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$.

In the dissociation of phosphorus pentachloride there is an increase in volume, and V now appears in the equation for the equilibrium constant :



In this case the volume, and hence the pressure, is involved. If V is increased, *i.e.* the pressure is decreased, the denominator in (ii) becomes too large and the numerator, and therefore x , must increase to keep the value of the expression on the right equal to K . Hence dissociation increases when the pressure is lowered. Similarly, it is shown that dissociation decreases when the pressure is raised. Dilution with an inert gas reduces the partial pressures of the reacting substances, and has the same effect as lowering the total pressure on the pure mixture.

Equation (ii) also applies to the case : $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, for which the effect of adding an inert gas was proved experimentally by Playfair and Wanklyn (1861).

Effect of change of temperature on equilibrium.—Unlike change of pressure, a change of temperature leads to a change in the value of the equilibrium constant K itself. The effect depends on the sign of the heat of reaction. In the equilibrium equation, reaction in one sense will evolve heat and reaction in the opposite sense will absorb heat. The general rule is that *rise of temperature favours that reaction which absorbs heat*. Hence, when the temperature of an equilibrium mixture is raised, that reaction takes place which tends to cool the system, *i.e.* which absorbs heat ; and when the temperature is lowered that reaction takes place which tends to heat the system, *i.e.* which evolves heat. Since the dissociation of HI , PCl_5 , and N_2O_4 absorbs heat, rise of temperature increases the extent of dissociation.

The effect of temperature can be calculated from the *reaction isochore equation*, due to van't Hoff (1885) :

$$\log K_2 - \log K_1 = \frac{q_v}{4.576} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where K_1 and K_2 are the equilibrium constants at the absolute temperatures

T_1 and T_2 , and q_p is the heat of reaction in gm. cal. absorbed at constant volume.

EXAMPLE.—The vapour densities (air = 1) of N_2O_4 and of the partly dissociated gas : $N_2O_4 \rightleftharpoons 2NO_2$, at 26.7° and 111.3° and 1 atm. pressure are 3.179, 2.65, and 1.65, respectively. The extent of dissociation x is calculated from the equation : $\alpha = (\Delta - D)/D$ (p. 116) as $(3.179 - 2.65)/2.65 = 0.1997$ at 26.7° , and $(3.179 - 1.65)/1.65 = 0.9266$ at 111.3° . The volume V containing $1 + x$ gm. mols. at 1 atm. at 26.7° is $22.4 \times 1.1997 \times (299.7/273) = 29.50$ lit., and at 111.3° is $22.4 \times 1.9266 \times (384.3/273) = 60.74$ lit. The equilibrium constant is $K = x^2/(1 - x)V$. Hence :

$$\log K_1 = \log [(0.1997)^2/0.8003 \times 29.50] = \bar{3}.2277$$

$$\log K_2 = \log [(0.9266)^2/0.0734 \times 60.74] = \bar{1}.2846$$

$$\therefore \log K_2 - \log K_1 = 2.0659.$$

$$\text{Also } 1/T_1 - 1/T_2 = (T_2 - T_1)/T_1 T_2 = 84.6/(299.7 \times 384.3) = 1/1359.5.$$

$$\text{Hence } q_p = 4.576 \times 2.0659 \times 1359.5 = 12,850 \text{ g. cal.}$$

Law of reaction.—The effects of changes of pressure and temperature on the composition of an equilibrium mixture are summarised in the law of reaction stated by Le Chatelier : *if a system in equilibrium is subjected to a constraint, a change occurs, if possible, of such a kind that the constraint is partly annulled.* This applies only to systems in equilibrium. Change of pressure leads to changes which alter the pressure in the opposite direction : changes of temperature lead to changes which tend, by absorption or evolution of heat, to changes of temperature in the opposite direction. In the last case, if the altered temperature be maintained, change of composition will occur in the specified sense. If a reaction occurs without change of volume, pressure has no influence; if it occurs without absorption or evolution of heat, temperature changes are without effect.

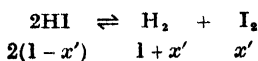
Effect of addition of products of reaction.—The effect of adding an excess of one of the products of dissociation *at constant volume* is easily seen from the law of mass action. In the dissociation of hydrogen iodide, to which the equation $K = [H_2] \times [I_2]/[HI]^2$ applies, addition of excess of hydrogen or iodine vapour increases the corresponding concentration, and to maintain the value of K , $[HI]$ must also increase, *i.e.* the extent of dissociation is reduced. The same result follows for the addition of phosphorus trichloride vapour or chlorine in the case of the dissociation of phosphorus pentachloride, $K = [PCl_3] \times [Cl_2]/[PCl_5]$.

The effect *at constant pressure* is not so easily seen, since the change of volume alters the concentrations.

Let 2 mols of hydrogen iodide be heated at 444° . Then (p. 294) :

$$x^2/4(1 - x)^2 = K = 0.01895$$

$\therefore x/(1 - x) = \pm \sqrt{(0.0758)} = \pm 0.2754$, and the admissible value of x is 0.216. Suppose 1 mol of hydrogen is added, the pressure remaining constant, and let x change to x' . Then :

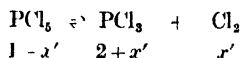


The total number of mols is $2(1 - x') + 1 + x' + x' = 3$, and the total volume is $V = 3RT/p$, where V is the volume at the temperature T and pressure p . Hence :

$$[HI] = 2(1 - x')p/3RT, \quad [H_2] = (1 + x')p/3RT, \quad [I_2] = x'p/RT, \\ \therefore K = x'(1 + x')/4(1 - x')^2 = 0.01895,$$

hence $x' = 0.063$ (the negative root being inadmissible). Since the degree of dissociation of pure HI at 444° is $x = 0.216$, the degree of dissociation is reduced by adding hydrogen at constant pressure. Addition of excess of iodine vapour would have the same effect.

Let 1 mol of PCl_5 be heated at 200° at 1 atm. pressure and let a further 2 mols of PCl_5 vapour be added at constant pressure. In PCl_5 vapour alone the degree of dissociation is 0.485, and $K = 0.00793$. Let x now change to x' . Then :



The total number of mols is $1 - x' + 2 + x' + x' = 3 + x'$, and the volume is $V = (3 + x')RT/p = (3 + x')RT$ ($p = 1$ atm.):

$$[PCl_5] = (1 - x')/RT(3 + x'), \quad [PCl_3] = (2 + x')/RT(3 + x'), \quad [Cl_2] = x'/RT(3 + x')$$

$$\therefore K = [PCl_3] \times [Cl_2]/[PCl_5] = x'(2 + x')/RT(3 + x')(1 - x') = 0.00793.$$

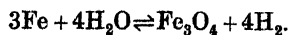
$$R = 0.08208 \text{ lit. atm./l}^\circ \text{ (p. 108), } T = 273 + 200 = 473, \therefore RT = 38.824,$$

$\therefore x'(2 + x')/(3 + x')(1 - x') = 0.3079$, $\therefore x' = 0.306$ (the other root being inadmissible). Hence the degree of dissociation is reduced from 0.485 to 0.3079.

Wurtz (1873) showed that when phosphorus pentachloride is volatilised in an atmosphere of phosphorus trichloride vapour at atmospheric pressure its dissociation is largely suppressed, very little of the colour of chlorine being seen. By volatilising phosphorus pentachloride and trichloride in a Dumas vapour density bulb, finding the density of the mixed vapour, and analysing the content of the bulb, he was able to calculate the vapour density of phosphorus pentachloride, which was nearly normal in presence of the excess of trichloride.

Heterogeneous equilibria.—Guldberg and Waage showed that when *solids* are present in a system their active masses may be taken as constant and included in the equilibrium constant K . In the reaction $K_2CO_3, Aq. + BaSO_4 \rightleftharpoons K_2SO_4, Aq. + BaCO_3$, the active masses of $BaSO_4$ and $BaCO_3$ may be taken as constant, hence $K = [K_2SO_4]/[K_2CO_3]$. This is easily understood, since the vapour pressure and solubility of a pure solid are constant at a given temperature, and in presence of the solid its concentration in the gas or solution is constant at that temperature.

As an example, consider the reaction :



Solid iron and the iron oxide may be supposed to have very small and constant vapour pressures, and hence to be present in the gas phase, too.

which the law of mass action applies, in very small and constant concentrations :

$$[\text{Fe}] = \text{const.}, [\text{Fe}_3\text{O}_4] = \text{const.}$$

The equilibrium in the gas phase is given by :

$$K' = [\text{Fe}_3\text{O}_4] \times [\text{H}_2]^4 / [\text{Fe}]^3 \times [\text{H}_2\text{O}]^4,$$

but since $[\text{Fe}_3\text{O}_4]/[\text{Fe}]^3$ is constant, this may be written :

$$K' = \text{const.} \times [\text{H}_2]^4 / [\text{H}_2\text{O}]^4$$

or

$$K = [\text{H}_2] / [\text{H}_2\text{O}],$$

showing that the ratio of the concentrations (or partial pressures) of hydrogen and steam is constant at a given temperature. This agrees with the experimental results. The equilibrium is not affected by the amounts of iron and iron oxide present.

Equilibrium constants in terms of partial pressures.—Since the *partial pressure* of a gas is simply related to its concentration, the law of mass action may be expressed in terms of partial pressures. Let n mols of a gas be contained in a volume V lit. The volume of 1 mol is V/n and the general gas equation (p. 107) may be written : $p(V/n) = RT$, or $p = (n/V)RT$. But $n/V =$ concentration c in mols per litre, hence $p = cRT$. A concentration c can, therefore, be replaced by p/RT , where p is the partial pressure of the gas in the mixture. The equilibrium constant is :

$$K = c_P^p c_Q^q \dots / c_A^a c_B^b \dots \\ = p_P^p p_Q^q \dots / (p_A^a p_B^b \dots \times (RT)^n),$$

where $n = p + q + \dots - (a + b + \dots)$. If :

$$K' = p_P^p p_Q^q \dots / p_A^a p_B^b \dots$$

is the equilibrium constant expressed in terms of partial pressures, this will be constant at a given temperature, since $(RT)^n$ and $K = K'/(RT)^n$ are constant at a given temperature. In most calculations the use of concentrations is more convenient and less likely to lead to error than when partial pressures are used.

Energy of activation.—Those molecules which are in a condition to undergo chemical change on collision (*active molecules*) appear to be those having more than the normal amount of vibrational energy corresponding with the temperature of the gas (see p. 117). To form an active molecule a *critical increment* of energy is necessary—

The number of bimolecular collisions per sec. in a mixture of hydrogen and iodine vapour can be calculated from the kinetic theory of gases, which also shows that it is proportional to \sqrt{T} (where $T =$ abs. temperature). Experiment shows that the rate of reaction is much smaller than it should be if every collision were effective, and also increases with temperature much faster than \sqrt{T} . The velocity of most reactions is about doubled for a rise of 10° . The results are explained by assuming that the proportion of active molecules increases with temperature by an exponential factor $e^{-g/kT}$, where k is Boltzmann's constant, or the gas constant per molecule,

$k = R/N$, where N is Avogadro's number, and q is the *energy of activation* (absorbed) per molecule. Per mol, the energy of activation is $Q = Nq$.

At 556° abs. the number of molecular collisions per sec. per lit. in hydrogen iodide at a concentration of 1 mol per litre is 6×10^{34} . The measured rate of decomposition into hydrogen and iodine is 2×10^{17} molecules per sec.

$$\therefore \frac{\text{no. of molecules decomposing per sec.}}{\text{no. of molecules colliding per sec.}}$$

$$\frac{2 \times 10^{17}}{6 \times 10^{34}} = e^{-Q/RT}$$

$$2.3026 \log_{10} \left(\frac{2 \times 10^{17}}{6 \times 10^{34}} \right) = -Q/(2 \times 556)$$

$$\therefore Q = 47,420 \text{ g. cal.}$$

(The value of R is taken as 2 g. cal./ 1° per mol). This is a large value as compared with ordinary heats of reaction (p. 282).

CHAPTER XIX

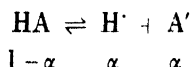
ELECTROLYTE EQUILIBRIA

THE study of *equilibria in electrolyte solutions* includes many topics of outstanding importance. We may state at the outset two fundamental assumptions underlying the whole treatment :

- (i) *Weak electrolytes obey the law of mass action in dilute solutions.*
- (ii) *Strong electrolytes are completely ionised and the law of mass action does not apply to them.*

Since most *salts* are strong electrolytes (p. 236) the application of the law of mass action to electrolytes is practically confined to *weak acids* and *weak bases*.

Ionisation of weak acids and bases.—The application of the law of mass action to weak acids and bases was made by Ostwald in 1888. Let 1 mol of a weak monobasic acid HA (*e.g.* acetic acid) be dissolved in V litres and let the degree of ionisation be α :



The concentrations are :

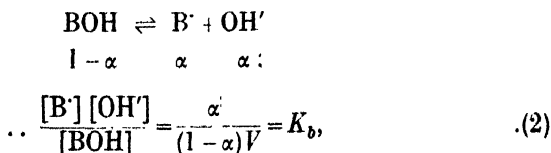
$$[\text{HA}] = (1 - \alpha)/V \quad [\text{H}^+] = \alpha/V \quad [\text{A}^-] = \alpha/V$$

and the law of mass action gives :

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{\alpha^2}{(1 - \alpha)V} = K_a, \dots\dots\dots (1)$$

where K_a is the *dissociation constant* of the weak acid.

Similarly for a weak monacid base such as ammonia NH_4OH :



where K_b is the dissociation constant of the base. Equation (1) or (2) is sometimes called *Ostwald's dilution law*.

The following results show that when α is calculated from the equivalent

conductivity, $\alpha = \lambda/\lambda_\infty$, the equations hold very accurately for acetic acid ($\lambda_\infty = 387$) and ammonia ($\lambda_\infty = 252$) at 25° :

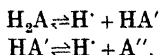
	V lit.	-	-	8	16	32	64	128	256
Acetic acid	λ	-	-	4.63	6.50	9.2	12.9	18.1	25.4
	100α	-	-	1.20	1.68	2.38	3.33	4.68	6.66
	$10^6 \times K_a$	-	-	18.1	17.9	18.1	18.0	17.9	18.0
Ammonia	λ	-	-	3.4	4.8	6.7	9.5	13.5	19.0
	100α	-	-	1.35	1.91	2.66	3.77	5.36	7.54
	$10^6 \times K_b$	-	-	23	23	23	23	24	24

For a weak electrolyte α is small compared with 1 and hence $(1 - \alpha)$ can be taken as unity in (1) and (2), giving:

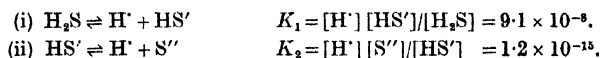
$$\alpha^2/V = \alpha^2 c = K; \quad \therefore \alpha = \sqrt{KV} = \sqrt{K/c}, \dots\dots\dots(3)$$

where $c = 1/V$ is the concentration. In a normal solution $\alpha = \sqrt{K}$.

The equations often apply to weak polybasic acids, which usually ionise in stages and only the first stage is appreciable except at very high dilutions. According to Ostwald the ionisation of the first (univalent) radical HA' of a dibasic acid begins to be appreciable only after 50 per cent of primary ionisation into H' and HA' :



A saturated solution of hydrogen sulphide at 25° is approximately 0.1 molar. It dissociates in two stages:



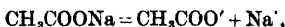
Both H_2S and HS' are very weak acids to which (1) applies, and the second dissociation constant is much smaller than the first.

An empirical method of determining the basicity of an acid, B , given by Ostwald (1887) depends on finding the equivalent conductivities of the sodium or potassium salt at dilutions of 32 and 1024 lit. at 25° and using the formula:

$$\lambda_{1024} - \lambda_{32} = 10.8B.$$

The common ion effect.—The law of mass action shows that the ionisation of a weak electrolyte HA or BOH is depressed by adding to the solution a largely ionised salt (MA or BX) containing an ion A' or B' present in the weak electrolyte solution. (The other ion of the salt is supposed to have no effect.)

By adding 0.1 mol (8.20 gn.) of solid sodium acetate CH_3COONa to 1 lit. of 0.1 molar acetic acid the total acetate ion concentration is approximately 0.1 mol/lit., since the sodium acetate is practically completely ionised:



and the concentration of acetate ions from the acetic acid is very small.

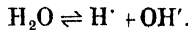
Hence $[CH_3COO'] \simeq 0.1$ and $[CH_3COOH] \simeq 0.1$, since the acid is only very slightly ionised. From (1) :

$$[H^+][CH_3COO']/[CH_3COOH] = 1.8 \times 10^{-5};$$

$$\therefore [H^+] \times 0.1/0.1 = 1.8 \times 10^{-5}, \quad \therefore [H^+] = 1.8 \times 10^{-5},$$

and since $[H^+] = \alpha c$, $\therefore \alpha = 1.8 \times 10^{-5}/0.1 = 1.8 \times 10^{-4}$. In 0.1 molar acetic acid alone (3) gives $\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = 1.34 \times 10^{-3}$. Thus, adding the sodium acetate has reduced the degree of ionisation from 1.34×10^{-3} to 1.8×10^{-4} .

Ionic product of water.—Pure water is only very slightly ionised.



The degree of ionisation can be found most accurately by the conductivity, and at 25° $[H^+] = [OH'] = 10^{-7}$ mol lit. Hence the mass-action equation gives

$$[H^+][OH']/[H_2O] = 10^{-14}, [H_2O] = K.$$

Since $[H_2O]$ is constant, $K[H_2O] = \text{const.} = K_w$, and

$$[H^+][OH'] = K_w \stackrel{2}{=} 10^{-14}, \dots\dots\dots(4)$$

where K_w is the *ionic product of water*. K_w increases with the temperature, and the reaction isochore equation (p. 294), with values of K_w at different temperatures, shows that the *heat of ionisation of water* = 13.48 k. cal. (absorbed) at 25°. This agrees with the value for the *heat of neutralisation* (p. 238), which is the heat evolved in the reverse reaction: $H^+ + OH' = H_2O$.

The ionic product of heavy water at 25° is $[D^+] \times [OD'] = 1.95 \times 10^{-15}$.

Hydrogen ion index or pH.—In all *neutral* solutions in water the hydrogen and hydroxide ion concentrations are equal: $[H^+] = [OH']$, but since (4) is also true for *all* solutions (acid, alkaline or neutral) the hydroxide ion concentration is always given by

$$[OH'] = K_w/[H^+] = 10^{-14}/[H^+]$$

at 25°, and alkaline solutions may be regarded as having hydrogen-ion concentrations smaller than 10^{-7} , *i.e.* having larger *negative* exponents. The whole range of reaction from acid to alkaline may thus be given in terms of the hydrogen ion concentrations or exponents.

Instead of the hydrogen ion concentration it is usual to give what is called the **pH value** for the solution, where

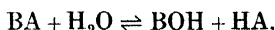
$$pH = -\log [H^+]. \dots\dots\dots(5)$$

Thus pH is the exponent of the hydrogen ion concentration (expressed as a power of 10) *with the sign changed*, or pH is *minus* the logarithm of the hydrogen ion concentration, or still again it is the logarithm of the *dilution* V lit. containing 1 mol of hydrogen ions (since $[H^+] = 1/V$). In *neutral* solutions $pH = -\log 10^{-7} = 7$, in *acid* solutions pH is *less* than 7,

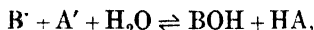
and in *alkaline* solutions pH is *greater* than 7. Strictly speaking pH is defined in terms of the hydrogen ion *activity* (p. 311) rather than the concentration :

$$\text{pH} = -\log a_{\text{H}^+} \dots\dots\dots(6)$$

Hydrolysis.—Salts of weak acids or weak bases or both are decomposed by water with formation of free acid and free base :



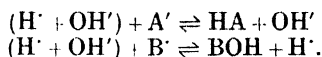
and the process, which is reversible, is called *hydrolysis*. Since the salt is practically completely ionised the equation may be written :



and either BOH or HA may be ionised if the base or acid is strong.

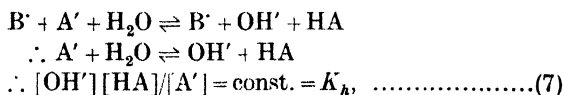
The following cases occur : (i) the acid HA is weak and the base BOH is strong, (ii) the base BOH is weak and the acid HA is strong, (iii) both the acid HA and the base BOH are weak.

Hydrolysis may also be regarded as due to the withdrawal of hydrogen ions from water by the anion of the weak acid, leaving hydroxide ions of water forming an alkaline solution ; or the withdrawal of hydroxide ions by the cation of the weak base, leaving hydrogen ions forming an acid solution :



The equations for hydrolysis are found by applying the law of mass action to the weak acid or base, or both ; the salt, strong acid and strong base being assumed completely ionised. It should be noted that the law of mass action must not be applied to a strong electrolyte.

(i) **Weak acid and strong base :**



where K_h is a constant. Since the base is strong ($\text{BOH} = \text{B}^+ + \text{OH}^-$), $[\text{OH}^-]$ is practically equal to [base], and since the salt is assumed completely ionised ($\text{BA} = \text{B}^+ + \text{A}^-$), $[\text{A}^-]$ is practically equal to [salt]. Hence (7) can be written :

$$\frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]} = K_h,$$

and K_h the *hydrolysis constant*.

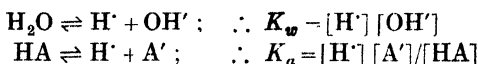
The *degree of hydrolysis* x is the fraction of each gm. mol. of salt hydrolysed at equilibrium. For 1 gm. mol. of salt in V litres

$$[\text{OH}^-] = [\text{HA}] = x/V \quad \text{and} \quad [\text{A}^-] = (1-x)/V ;$$

\therefore from (7)

$$K_h = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{(x/V) \times (x/V)}{(1-x)V} = \frac{x^2}{(1-x)V} \dots\dots\dots(8)$$

This shows that the degree of hydrolysis x increases with the dilution V . In the solution there are two equilibria holding simultaneously :



\therefore from (7) :

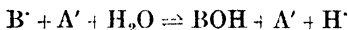
$$K_w = \frac{[\text{H}^+][\text{OH}']}{[\text{H}^+]} = \frac{[\text{OH}']}{[\text{H}^+]} = \frac{[\text{OH}']}{[\text{A}']} \frac{[\text{HA}]}{[\text{A}']} = K_h \dots\dots\dots(9)$$

$$\therefore K_h = K_w/K_a \dots\dots\dots(10)$$

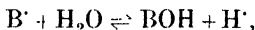
The hydrogen ion concentration $[\text{H}^+]$ (or $\text{pH} = -\log [\text{H}^+]$) is found as follows. If $c = 1/V = \text{total salt concentration in mols/lit.}$, then since $[\text{HA}] = [\text{OH}']$, and $\text{p}x = -\log x$ where x is any number :

$$\begin{aligned} [\text{HA}][\text{OH}']/[\text{A}'] &= K_h = [\text{OH}']^2/c \\ \therefore \text{from (10)} \quad [\text{OH}']^2/c &= K_w/K_a \\ \therefore [\text{OH}'] &= \sqrt{cK_w/K_a} ; \quad \therefore [\text{H}^+] = K_w/[\text{OH}'] = \sqrt{K_wK_a/c} ; \\ \therefore \text{pH} &= \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c \dots\dots\dots(11) \end{aligned}$$

(ii) Weak base and strong acid:

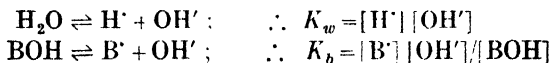


or



$$K_h = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}']} = \frac{[\text{acid}][\text{base}]}{[\text{unhydrolysed salt}]}$$

Also



$$\therefore K_h = K_w/K_b \dots\dots\dots(12)$$

and

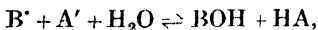
$$[\text{H}^+] = [\text{BOH}] = x/V, \quad [\text{B}'] = (1-x)/V,$$

$$\therefore K_h = \frac{K_w}{K_b} = \frac{x^2}{(1-x)V} \dots\dots\dots(13)$$

Again, $K_h = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}']} = \frac{[\text{H}^+]^2}{c} ; \quad \therefore [\text{H}^+] = \sqrt{cK_w/K_b}$

$$\therefore \text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \dots\dots\dots(14)$$

(iii) Weak acid and weak base:

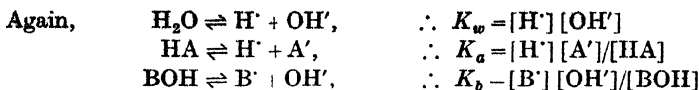


$$K_h = \frac{[\text{BOH}][\text{HA}]}{[\text{B}'][\text{A}']} = \frac{[\text{base}][\text{acid}]}{[\text{unhydrolysed salt}]^2}$$

$$[\text{BOH}] = [\text{HA}] = x/V, \quad [\text{B}'] = [\text{A}'] = (1-x)/V ;$$

$$\therefore K_h = \frac{(x/V) \times (x/V)}{\{(1-x)/V\}^2} = \frac{x^2}{(1-x)^2} \dots\dots\dots(15)$$

In this case the degree of hydrolysis is independent of the dilution, V .



$$\therefore K_w = \frac{[\text{BOH}][\text{HA}]}{[\text{B}^+][\text{A}^-]} = K_a K_b, \dots\dots\dots(16)$$

Also $[\text{H}^+] = K_a[\text{HA}]/[\text{A}^-] = K_a \frac{x/V}{(1-x)/V} = K_a \frac{x}{1-x},$

and since $x/(1-x) = \sqrt{K_h}$ from (15),

$$\begin{aligned} \therefore [\text{H}^+] &= K_a \sqrt{K_h} = \sqrt{K_w K_a / K_b}, \\ \therefore \text{pH} &= \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b. \dots\dots\dots(17) \end{aligned}$$

As examples of hydrolysis we may cite potassium cyanide, a salt of the weak hydrocyanic acid: $\text{KCN} + \text{H}_2\text{O} = \text{K}^+ + \text{OH}^- + \text{HCN}$, giving an alkaline solution smelling of hydrocyanic acid; and aniline hydrochloride, a salt of the weak base aniline, giving an acid solution containing hydrochloric acid and free aniline.

(i) In 0.01 molar *sodium acetate* solution at 25°:

$$K_h = K_w/K_a = 10^{-14}/1.82 \times 10^{-5} = 5.5 \times 10^{-10}.$$

The degree of hydrolysis x is given by $K_h = x^2/(1-x)V = x^2c/(1-x)$;

$$\therefore 5.5 \times 10^{-10} = x^2 \times 0.01/(1-x); \quad \therefore x = 0.000235.$$

From (11): $\text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c = 7 + 2.37 + \frac{1}{2}(-2) = 8.37.$

The *equivalence point* in the titration of acetic acid by NaOH (*i.e.* when chemically equivalent amounts have been mixed, *e.g.* 10 ml. of *N/10* acetic acid and 10 ml. of *N/10* NaOH) is not the same as the *neutral point* ($\text{pH} = 7$), because the solution is alkaline from the hydrolysis of the sodium acetate, and in the titration a suitable indicator which changes on the alkaline side ($\text{pH} > 7$) must be used.

(ii) In 0.2 molar *ammonium chloride* at 25°, from (14):

$$\text{pH} = 7 - 2.37 - \frac{1}{2}(-0.70) = 4.98.$$

At the equivalence point in the titration of ammonia with hydrochloric acid the solution is distinctly acid ($\text{pH} < 7$) and an indicator which changes colour in the acid region must be used, *e.g.* methyl orange or methyl red, but not phenolphthalein.

Buffer solutions.—A solution containing a weak acid or base and a salt of this with a strong base or acid, respectively, has the following properties:

(i) it has a definite pH value determined by the ratio

$$[\text{acid}]/[\text{salt}] \quad \text{or} \quad [\text{base}]/[\text{salt}];$$

(ii) the pH value is practically unchanged by dilution;

(iii) the pH value is only slightly changed by addition of a strong acid in the case of the weak acid mixture or of a strong base in the case of the weak base mixture.

Such a solution is called a *buffer solution*. Examples are a mixture of acetic acid and sodium acetate solution, and of ammonia and ammonium chloride solution.

If to acetic acid of concentration $[HAc]$ solid sodium acetate is added to concentration $[NaAc]$ we can assume the sodium acetate completely ionised, $\therefore [Ac'] = \text{total NaAc concentration} = [\text{salt}]$, the acetate ions from the weak acetic acid in presence of the salt being negligible. For the acetic acid :

$$[H^+][Ac']/[HAc] = K_a$$

$$\therefore [H^+] = K_a [HAc]/[Ac'] = K_a \frac{[\text{acid}]}{[\text{salt}]}$$

Since the ratio $[\text{acid}]/[\text{salt}]$ is practically not changed by dilution (the ionisation of the acid remaining practically constant), the hydrogen ion concentration is also constant. By taking logarithms :

$$\log [H^+] = \log K_a + \log \frac{[\text{acid}]}{[\text{salt}]}$$

and putting $p_x = -\log x$ we find

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}, \quad (18)$$

which is the *Henderson and Hasselbalch equation*.

Suppose solid sodium acetate is added to 1 lit. of $N/10$ acetic acid to make the solution $N/10$ in sodium acetate. Then $[Ac'] = 0.1$, hence at 18° :

$$[H^+] = K_a [HAc]/[Ac'] = 1.8 \times 10^{-5} \times 0.1/0.1 = 1.8 \times 10^{-5}$$

or

$$pH = -\log (1.8 \times 10^{-5}) = 4.74.$$

Now add 10 ml. of N hydrochloric acid and neglect the volume change from 1000 to 1010 ml. The hydrochloric acid takes acetate ions and forms practically undissociated acetic acid :

$$\therefore [Ac'] = 0.1 - 0.01 = 0.09,$$

$$[HAc] = 0.1 + 0.01 = 0.11;$$

$$\therefore [H^+] = K_a [HAc]/[Ac'] = 1.8 \times 10^{-5} (0.11/0.09) = 2.2 \times 10^{-5}$$

or $pH = 4.66$. Hence on adding the strong acid the pH changes only by

$$4.74 - 4.66 = 0.08 \text{ unit,}$$

whereas if the 10 ml. of N HCl had been added to a litre of pure water ($pH \approx 7$) the pH would have changed to $-\log (0.01) = 2$, i.e. by 5 units.

A mixture of ammonia and ammonium chloride is used in qualitative analysis because the OH' concentration has a small value which is

sufficient to precipitate hydroxides of Group III metals but not of Group IV metals. In this case it is easily shown that :

$$[\text{OH}'] = K_b \frac{[\text{base}]}{[\text{salt}]},$$

$$\therefore \text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}, \dots\dots\dots(19)$$

since $K_b = [\text{B}'] [\text{OH}'] / [\text{BOH}]$ and $[\text{B}'] \simeq [\text{salt}]$.

Another weak acid buffer solution contains Na_2HPO_4 and KH_2PO_4 , which are practically completely ionised, so that

$$[\text{HPO}_4''] \simeq [\text{Na}_2\text{HPO}_4] \quad \text{and} \quad [\text{H}_2\text{PO}_4'] \simeq [\text{KH}_2\text{PO}_4].$$

Also $\text{H}_2\text{PO}_4' \rightleftharpoons \text{H}^+ + \text{HPO}_4''$

$$\therefore [\text{H}^+] = K_2 \frac{[\text{H}_2\text{PO}_4']}{[\text{HPO}_4'']}$$

where $K_2 = 7.4 \times 10^{-8}$ is the second dissociation constant of phosphoric acid.

$$\text{Hence} \quad \text{pH} = \text{p}K_2 - \log \frac{[\text{Na}_2\text{HPO}_4]}{[\text{KH}_2\text{PO}_4]}.$$

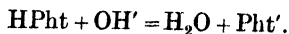
(See Partington and Stratton, *Intermediate Chemical Calculations*, Chap. XII.)

Some simple buffer solutions are made up from the following solutions : 0.1N acetic acid, 0.1N hydrochloric acid, 0.1N sodium hydroxide ; 35.5 gm. crystalline sodium phosphate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in 1 litre ;

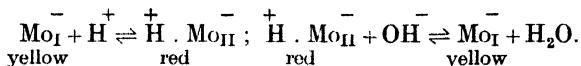
[H ⁺]	pH	Composition of solution
10 ⁻³	3	142.5 ml. acetic acid + 107.5 ml. water
10 ⁻⁴	4	2.7 gm. cryst. sodium acetate ($\text{C}^2\text{H}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) in 1 litre + 1 litre acetic acid
10 ⁻⁵	5	15 gm. cryst. sodium acetate in 500 ml. + 500 ml. acetic acid
10 ⁻⁶	6	300 ml. sodium phosphate + 250 ml. 0.1N HCl
10 ⁻⁷	7	234 ml. sodium phosphate + 184 ml. 0.1N HCl
10 ⁻⁸	8	200 ml. sodium phosphate + 9.4 ml. 0.1N HCl
10 ⁻⁹	9	200 ml. sodium phosphate + 1.0 ml. 0.1N HCl
10 ⁻¹⁰	10	200 ml. sodium phosphate + 0.72 ml. 0.1N NaOH
10 ⁻¹¹	11	200 ml. sodium phosphate + 7.2 ml. 0.1N NaOH.

Indicators.—According to Ostwald (1891) indicators are weak acids or weak bases which have different colours in the undissociated and dissociated states. In many cases, as Haantzsch (1908) showed, the coloured ion may have a different structure from the original indicator molecule, but this does not affect the general principle.

Phenolphthalein is a very weak acid and is colourless when non-ionised. In presence of alkali a salt is formed which is largely ionised to give an intensely red anion :



Methyl orange is the sodium salt of a sulphonic acid and is largely ionised in solution. The yellow anion in presence of acids behaves as a weak base, attaches a hydrogen ion H^+ and rearranges to form a red ion which has opposite charges on different parts but is electrically neutral as a whole (a *hybrid ion*). In presence of alkalis this gives the yellow anion :



If we consider an indicator which behaves as a weak acid dissociating to the extent α and neglect the structure changes (which do not affect the final equations) we have :

$$[H^+][A^-]/[HA] = K_a = [H^+] \frac{\alpha}{1 - \alpha}$$

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}, \quad (20)$$

hence when $\alpha = 0.5$, $pH = pK_a$.

The curves of α plotted against pH are all of the same form (Fig. 168). For pH less than 5 the given indicator is hardly ionised and shows no colour change ; the change occurs in the pH range 6 to 8. The pH ranges in which various indicators change colour are shown in Fig. 169. The gaps are to be filled in with the adjoining colour, e.g. phenolphthalein is colourless for $pH < 8$. Thymol blue has two colour ranges.

When the colour range is narrow the indicator change is sharp. The pH value at which the sharpest colour change occurs is called the *indicator exponent* pT.

This is, for methyl orange 4, for methyl red 5, and for phenolphthalein 8.

Indicators are thus weak acids or weak bases which change colour in a definite pH range, and an ion of the indicator has a different colour from the indicator molecule.

An example of a *screened indicator* is a mixture of methyl orange and indigo-carmin which is yellowish-green in alkaline solution and changes through grey at $pH = 4$ to violet. A *universal indicator* is a mixture of several indicators giving a range of colours for a succession of pH values.

Choice of an indicator.—In acidimetry and alkalimetry the *choice of indicator* depends on the hydrogen-ion concentration of the resulting salt. If a slightly alkaline salt like sodium acetate is formed at the *equivalence point* (when equivalent amounts of acid and base are present ; this is not the same as the *neutral point* if there is hydrolysis) an indicator is used which shows a change of colour on the alkaline

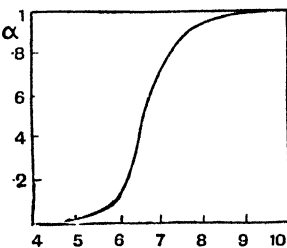


FIG. 168. Ionisation of indicator.

side over a pH range including the pH value of the equivalence point. Phenolphthalein, which changes colour for pH about 8 to 10, is therefore used in titrating acetic acid with sodium hydroxide. If a weak base like ammonia is titrated with a strong acid, the resulting acid-reacting salt will require an indicator which changes colour over the

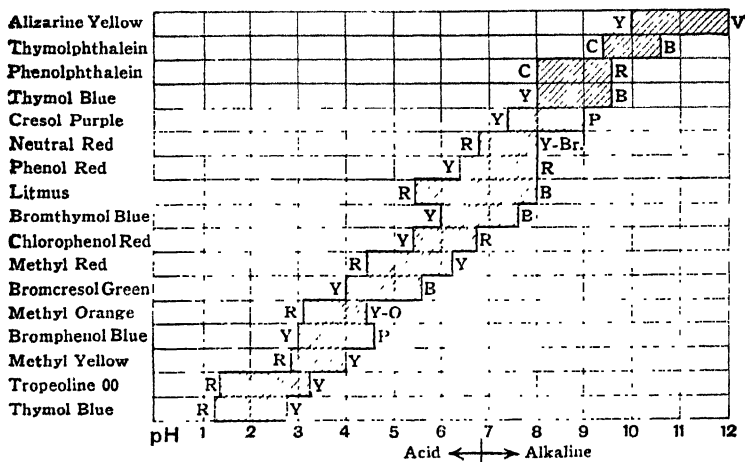


FIG. 169.—pH intervals of indicators.

Y = yellow. V = violet. B = blue. C = colourless. R = red.
P = purple. Br = brown. O = orange.

appropriate pH range on the acid side. In this case methyl red, which changes at pH about 4 to 6, may be used. When a neutral salt is formed, as in titrating a strong acid with a strong base, a slight excess of either solution makes a large change in pH, so that any indicator having a colour change between pH 3 and 10 will be satisfactory. Conversely, the titration of a very weak base with a very weak acid is seldom possible on account of the relatively small change in pH value at the end-point (see p. 310).

Titration curves.—The plots of the pH values of solutions in acid-alkali titrations against volume of acid or alkali added are called *titration curves*, and are important in giving the pH at the equivalence point and so enabling suitable indicators to be chosen. Some of these curves are shown in Fig. 170 (temperature 25°).

(1) *Strong acid and strong base.*—Suppose we take 100 ml. of *N* HCl and add *x* ml. of *N* NaOH. The un-neutralised acid is (100 - *x*) and the volume (100 + *x*) ml.; ∴ $[H^+] = (100 - x)/(100 + x)$. The pH = -log $[H^+]$ values are :

<i>x</i>	50	75	90	98	99	99.9
pH	0.48	0.85	1.3	2.0	2.3	3.3

For $x = 100$ (equivalence point), $\text{pH} = 7.0$, the neutral point, since the acid and base are strong. For x greater than 100 the solution is alkaline. *E.g.* with $x = 100.1$, $[\text{OH}'] = 0.1/200.1 = 5.0 \times 10^{-4}$; $\therefore \text{pOH} = 3.3$ and $\text{pH} = 14.0 - 3.3 = 10.7$, since $[\text{H}'] [\text{OH}']$ at 25° is 10^{-14} . There is a very sudden rise in pH as x changes from 99.9 to 100.1, and many suitable indicators may be chosen in the range 3.3 to 10.7.

The second part of the curve is calculated from the values :

x	100.1	100.5	101	110	150	200
pH	10.7	11.4	11.7	12.7	13.3	13.5

Similar curves may be plotted for 0.1*N* and 0.01*N* solutions, when it will be found that the rising part is shorter and hence there is less choice of

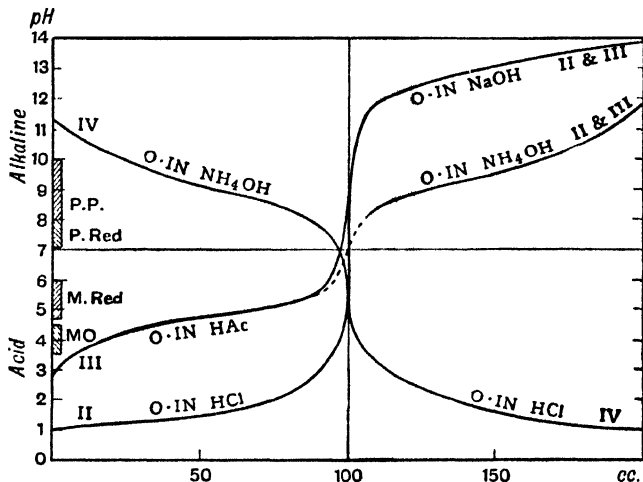


FIG. 170.--Titration curves.

indicators. Curves for 0.1*N* solutions are shown in Fig. 170. In this case $[\text{H}'] = 0.1(100 - x)/(100 + x)$ for $x < 100$ and $[\text{OH}'] = 0.1(x - 100)/(100 + x)$ for $x > 100$, and it is clear that the pH values are found by adding unity ($-\log 0.1$) to the pH values of *N* solutions given above for $x < 100$, and subtracting unity for values of $x > 100$. The resulting curve is II in Fig. 170.

(2) *Weak acid and strong base.*—For the titration of 100 ml. of 0.1*N* acetic acid with x ml. of 0.1*N* NaOH we find pH for the equivalence point ($x = 100$) by equation (11) with $K_a = 1.82 \times 10^{-5}$ and $c = 0.05$:

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2} \log c = 7 + 2.37 + \frac{1}{2}(-1.3) = 8.72.$$

For other values of x equation (18) gives :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \dots\dots\dots(18)$$

The initial pH is found from (1) :

$$[\text{H}'] [\text{Ac}'] / \text{HAc} = [\text{H}']^2 / 0.1 = 1.82 \times 10^{-5} ;$$

$$\therefore [\text{H}'] = \sqrt{1.82 \times 10^{-6}} = 1.35 \times 10^{-3} ; \therefore \text{pH} = 2.87.$$

When x ml. of 0.1*N* alkali are added, $[\text{salt}] = x \times 0.1 / (100 + x)$, and

$$[\text{acid}] = (100 - x) \times 0.1 / (100 + x),$$

from which pH is found from (18). The values are plotted as curve III (Fig. 170). For $x > 100$ it may be assumed that the excess of alkali represses the hydrolysis of the salt, and this part of the curve thus coincides with that of case (1), viz. the alkaline side of curve II.

x	0	10	25	50	90	99	99.9	100
pH	2.87	3.8	4.3	4.7	5.7	6.7	7.7	8.87

The curves for a weak base and a strong acid (e.g. NH_4OH , $K_b = 1.8 \times 10^{-5}$, and HCl) shown in IV, and for a weak acid and a weak base (e.g. acetic acid and ammonia) shown in III, are constructed in a similar way.

Polybasic acids have separate dissociation constants for each stage of ionisation, e.g. phosphoric acid (tribasic) has :

$$[\text{H}^+][\text{H}_2\text{PO}_4'] / [\text{H}_3\text{PO}_4] = K_1 = 8.0 \times 10^{-3},$$

$$[\text{H}^+][\text{HPO}_4''] / [\text{H}_2\text{PO}_4'] = K_2 = 7.4 \times 10^{-8},$$

$$[\text{H}^+][\text{PO}_4'''] / [\text{HPO}_4''] = K_3 = 4.8 \times 10^{-13}.$$

In such cases the titration curve is formed by superposing the curves plotted for each dissociation separately, provided the dissociation constants are well separated, since each stage of dissociation does not become appreciable until the preceding stage is practically complete.

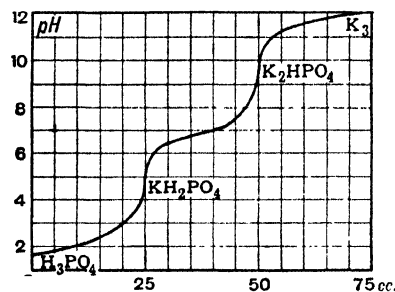


FIG. 171.—Titration curve for phosphoric acid.

able until the preceding stage is practically complete.

The curve is shown in Fig. 171, and it is seen that the end-points for the first two stages, KH_2PO_4 and K_2HPO_4 , may be found with suitable indicators, but not the third stage (K_3PO_4), when the liquid is strongly alkaline. The correct end-point for KH_2PO_4 (or NaH_2PO_4) is when a little orange colour remains with methyl orange, but the next drop of 0.1*N* alkali (not counted)

gives a pale yellow; the end-point for Na_2HPO_4 is when the last drop (counted) of 0.1*N* alkali gives a full red colour with phenolphthalein.

Strong electrolytes.—The law of mass action does not apply to strong electrolytes, which are considered to be completely ionised in dilute solutions. In more concentrated solutions ion pairs are formed, but these are not true covalent molecules like those of weak electrolytes. Hence an equation similar to (1) does not apply to, say, potassium chloride, as the following figures show, α being assumed to be given by λ/λ_∞ :

$c = 1/V$ mols per lit.	10^5	10^{-3}	10^{-1}	1
$\alpha = \lambda/\lambda_\infty$	0.994	0.980	0.862	0.757
$K = \alpha^2/c(1 - \alpha)$	0.0016	0.048	0.55	2.36

It is now believed that $\alpha = 1$ throughout and K has no meaning, since α is not now given by λ/λ_∞ (p. 229).

G. N. Lewis introduced the useful idea of the *activity* of a solute, this being a quantity a which plays the same part as the concentration c in ideal solutions (obeying the gas laws) and is equal to c at infinite dilution. Thus for a strong electrolyte giving two univalent ions: $MA = M^+ + A^-$, we may define the activities by the equation:

$$a_+ a_- = a^2, \dots\dots\dots(21)$$

where a_+ , a_- are the activities of the ions, a the *mean activity* of the electrolyte. The ratio a/c is called the *activity coefficient* f :

$$a/c = f, \dots\dots\dots(22)$$

which varies with the concentration of the ions; at infinite dilution the value of f is unity. Hence:

$$(f_+ c_+) (f_- c_-) = (fc)^2, \dots\dots\dots(23)$$

where f is the activity coefficient of the electrolyte of concentration c .

The activity coefficients of the ions depend on the *total ion concentration*, including ions of other salts present. For a solid salt in equilibrium with its saturated solution, the activity of the dissolved salt is constant at a given temperature, but it is found that the solubility c increases if another salt having no ions in common with the first is present in solution. Since fc is constant it follows that f must vary. Debye and Hückel in 1923 showed that the activity coefficient of a given salt (electrolyte) in very dilute solution in water at 25° is given by:

$$\log f = 0.5 z_+ z_- \sqrt{I}, \dots\dots\dots(24)$$

where I is the *ionic strength*:

$$I = \frac{1}{2} \sum c_i z_i^2, \dots\dots\dots(25)$$

and depends on the concentrations c_i and valencies z_i of *all* the ions in solution. In (24) z_+ and z_- are the valencies of the ions of the given salt with proper signs ($z_+ z_-$ is negative).

For a completely ionised electrolyte giving univalent ions:

$$c_+ = c_- = c, \text{ the total concentration;}$$

$$\therefore I = \frac{1}{2} \sum c_i z_i^2 = \frac{1}{2} (c_+ + c_-) = \frac{1}{2} (2c) = c,$$

i.e. the ionic strength is equal to the total concentration. Hence the activity coefficient of 0.01N KCl at 25° is given by:

$$\begin{aligned} \log f &= 0.5 z_+ z_- \sqrt{I} \\ &= -0.5 \sqrt{0.01} \\ &= -0.05 = -1 + 0.95; \\ \therefore f &= \text{antilog}(\bar{1}.95) = 0.891. \end{aligned}$$

For completely ionised barium chloride in 0.01 molar solution at 25° ($\text{Ba}^{++} + 2\text{Cl}'$), $c_+ = c$, $c_- = 2c$, $z_+ = 2$, $z_- = -1$;

$$\therefore I = \frac{1}{2}[2^2c + (-1)^22c] = 3c = 0.03,$$

$$\therefore \sqrt{I} = 0.173,$$

$$\therefore \log f = 0.5z_+z_- \sqrt{I} = 0.5 \times 2 \times (-1) \times 0.173 = -0.173$$

$$= \bar{1}.827,$$

$$\therefore f = \text{antilog } \bar{1}.827 = 0.67.$$

Solubility product.—In a very dilute solution of a strong electrolyte BA in pure water the substance is assumed to be completely ionised: $\text{BA} = \text{B}' + \text{A}'$, and if S_0 is the solubility of BA in gm. mol. per litre, $S_0 = [\text{B}']_0 = [\text{A}']_0$, i.e. S_0 is equal to each separate ion concentration. The *ionic concentration product* is:

$$[\text{B}']_0 \times [\text{A}']_0 = S_0^2 = K_s \dots\dots\dots(25)$$

where K_s is called the *solubility product*; for any solute and solvent it depends on the temperature.

If another electrolyte CA, having an ion A in common with the first, is added to the saturated solution of BA, the *solubility product principle* states that the ionic concentration product of BA still has the same value:

$$[\text{B}'] \times [\text{A}'] = [\text{B}']_0 \times [\text{A}']_0 = S_0^2 \dots\dots\dots(26)$$

Since $[\text{A}']$ has increased, $[\text{B}']$ must have decreased, and the only way in which this can have happened is by some BA going out of solution. Hence the solubility of BA has been reduced to S , less than S_0 . Since the values of $[\text{A}']$ and S_0 are known, the value of $[\text{B}']$ may be calculated, and as $[\text{B}']$ is equal to the total concentration S of completely ionised BA, the value of S can be calculated.

For an electrolyte B_pA_q giving p positive ions and q negative ions, the solubility product is:

$$[\text{B}']^p \times [\text{A}']^q = \text{const.} = S_0^{p+q}.$$

If to a saturated solution of silver acetate, (a) concentrated silver nitrate, (b) saturated sodium acetate, solutions are added, then in both cases silver acetate is precipitated.

Some values of the solubility product for sparingly soluble electrolytes at 25° are given below.

$[\text{Ag}'] [\text{Cl}']$	1.2×10^{-10}	$[\text{Ca}^{++}] [\text{C}_2\text{O}_4^{--}]$	3.8×10^{-9}
$[\text{Ag}'] [\text{Br}']$	3.5×10^{-13}	$[\text{Ba}^{++}] [\text{SO}_4^{--}]$	1.2×10^{-10}
$[\text{Ag}'] [\text{I}']$	1.7×10^{-16}	$[\text{Cu}'] [\text{I}']$	2.6×10^{-12}
$[\text{Ca}^{++}] [\text{CO}_3^{--}]$	7.2×10^{-9}	$[\text{Pb}^{++}] [\text{CrO}_4^{--}]$	1.8×10^{-14}
$[\text{Ca}^{++}] [\text{SO}_4^{--}]$	2.3×10^{-4}	$[\text{Pb}^{++}] [\text{SO}_4^{--}]$	2.3×10^{-8}

[Mn ⁺⁺][S ^{''}]	1.4 × 10 ⁻¹⁵	[Fe ^{''}][OH'] ²	1.6 × 10 ⁻¹⁴
[Fe ^{''}][S ^{''}]	1.5 × 10 ⁻¹⁹	[Fe ^{'''}][OH'] ³	1.1 × 10 ⁻³⁶
[Zn ⁺⁺][S ^{''}]	1.0 × 10 ⁻²⁰	[Mg ^{''}][OH'] ²	2.5 × 10 ⁻¹³
[Pb ⁺⁺][S ^{''}]	5.0 × 10 ⁻²⁰	[Mn ^{''}][OH'] ²	4.0 × 10 ⁻¹⁴
[Hg ⁺⁺][S ^{''}]	4.0 × 10 ⁻⁵²	[Ni ^{''}][OH'] ²	8.7 × 10 ⁻¹⁹

EXAMPLE 1.—Calculate the solubility of silver chloride at 25° if the solubility product is 1.2×10^{-10} . Since the solubility is small, the silver chloride is almost completely ionised, hence if the solubility is S gm. mols. per lit.

$$[\text{Ag}'] = [\text{Cl}'] = S; \quad \therefore S^2 = K_s;$$

$$\therefore S = \sqrt{K_s} = \sqrt{1.2 \times 10^{-10}} = 1.095 \times 10^{-5} \text{ gm. mols. per lit.}$$

EXAMPLE 2.—Solid silver chloride is shaken with 1 lit. of sodium chloride solution containing 3 gm. of the salt. If the solubility product of AgCl at the temperature of the experiment is 9×10^{-11} and the NaCl is completely ionised, how many gm. of AgCl will dissolve?

$$3 \text{ gm. of NaCl} = 3/58.5 = 5.13 \times 10^{-2} \text{ gm. mols.};$$

$$\therefore [\text{Cl}'] \text{ from NaCl} = 5.13 \times 10^{-2} \text{ gm. mols./lit.}$$

Let x gm. mols. of AgCl dissolve. This forms x gm. mols. of Ag' and Cl', since it is assumed completely ionised. Hence in the solution $[\text{Ag}'] = x$ and $[\text{Cl}'] = 5.13 \times 10^{-2} + x$; $\therefore x(x + 5.13 \times 10^{-2}) = K_s = 9 \times 10^{-11}$. Since x^2 may be neglected in comparison with x , $5.13 \times 10^{-2}x = 9 \times 10^{-11}$, $\therefore x = 1.75 \times 10^{-9}$ gm. mols./lit., or

$$1.75 \times 10^{-9} \times 143.38 = 2.5 \times 10^{-7} \text{ gm./lit.}$$

In very dilute solutions the solubility product principle gives satisfactory results, as is seen from the following figures (concentrations in gm. mols. per litre) for silver nitrite.

Conc. of AgNO ₃ or KNO ₃	Solubility of AgNO ₂ in presence of		Solubility calcd.
	AgNO ₃	KNO ₃	
0	0.0269	0.0269	0.0269
0.00258	0.0260	0.0259	0.0257
0.00588	0.0244	0.0249	0.0241
0.02355	0.0192	0.0203	0.0176

In such dilute solutions the activity coefficients are practically unity, so that the principle (which holds strictly only for *activities*) will hold very closely for concentrations:

$$a_+^p a_-^q = c_+^p f_+^p \cdot c_-^q f_-^q \simeq c_+^p c_-^q = \text{const.}$$

Precipitation of sulphides.—An important application of the solubility product principle is in the *precipitation of sulphides of metals* in qualitative analysis.

A saturated solution of hydrogen sulphide at 25° is about 0.1 molar. The first and second dissociation constants (p. 310) are :

$$[H^+][HS']/[H_2S] = 9.1 \times 10^{-8} \text{ and } [H^+][S'']/[HS'] = 1.2 \times 10^{-15}.$$

With $[H_2S] = 0.1$ and $[H^+] = [HS']$ (neglecting the very small ionisation of HS'),

$$[H^+][HS'] = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.5 \times 10^{-5},$$

hence $[S''] = 1.2 \times 10^{-15} \times 9.5 \times 10^{-5} / 9.5 \times 10^{-5} = 1.2 \times 10^{-15}$.

In 0.25 molar HCl (assumed completely dissociated) the solubility of H_2S is approximately the same as in water, but the ion concentrations are much reduced. We now have $[H^+] = 0.25$,

$$\therefore [HS'] = 9.1 \times 10^{-8} [H_2S] / [H^+] = 9.1 \times 10^{-8} \times 0.1 / 0.25 = 3.6 \times 10^{-8}$$

and $[S''] = 1.2 \times 10^{-15} [HS'] / [H^+] = 1.2 \times 10^{-15} \times 3.6 \times 10^{-8} / 0.25 = 1.7 \times 10^{-22}$.

The solubility product of ZnS is 1.0×10^{-20} ; \therefore in 0.1 molar solution of a zinc salt (assumed completely ionised) in a saturated solution of hydrogen sulphide in water $[Zn^{2+}] \times [S''] = 0.1 \times 1.2 \times 10^{-15} = 1.2 \times 10^{-16}$. This is greater than the solubility product, hence some ZnS is precipitated. The precipitation is incomplete, because the hydrogen ions formed by the reaction $Zn^{2+} + H_2S = ZnS + 2H^+$ accumulate in the solution and reduce the value of the sulphide ion concentration $[S'']$ by mass action to a value lower than corresponds with the solubility product $[Zn^{2+}] \times [S''] = 1.0 \times 10^{-20}$. In a solution of H_2S in 0.25 molar HCl, the sulphide ion concentration is $[S''] = 1.7 \times 10^{-22}$, and if the solution is molar in zinc ion concentration,

$$[Zn^{2+}] \times [S''] = 0.1 \times 1.7 \times 10^{-22} = 1.7 \times 10^{-23},$$

which is below the solubility product value, and hence zinc sulphide is not precipitated.

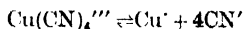
The solubility products of CuS, HgS, PbS, and CdS are all much smaller than 10^{-23} , hence these are precipitated in the acid solution. If sodium acetate is added, or if ammonium sulphide in alkaline solution is used as a precipitant, the value of $[H^+]$ is kept low, hence $[S'']$ increases and the solubility products of ZnS, MnS, etc., are exceeded, and these sulphides are precipitated.

The *solubility of metal sulphides*, etc. in acids may be explained on similar grounds.

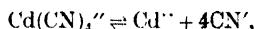
A trace of sulphide is soluble in water and ionises, e.g. $FeS = Fe^{2+} + S''$, and its sulphide ion S'' combines with the hydrogen ions of the acid to form the weakly ionised hydrogen sulphide: $S'' + 2H^+ \rightleftharpoons H_2S$. Then more sulphide dissolves. If it is one of the more soluble sulphides (ZnS, MnS, FeS) its solubility product is not exceeded even in acid saturated with H_2S (giving the maximum S'' ion concentration), so that hydrogen sulphide gas escapes and the sulphide dissolves as long as acid is present in excess. With very slightly soluble sulphides (PbS, CuS, HgS) the solubility product is exceeded before the solution is saturated with H_2S , and the sulphide is not dissolved.

Complex ions.—Silver chloride dissolves in ammonia to form the complex ion $\text{Ag}(\text{NH}_3)_2'$, and silver cyanide dissolves in alkali cyanide solution to form the complex ion $\text{Ag}(\text{CN})_2'$. A complex ion is formed by the combination of a simple ion with neutral molecules or other ions of opposite charge. The stability of complex ions varies a good deal according to their character. The complex ion $\text{Ag}(\text{CN})_2'$ is slightly dissociated: $\text{Ag}(\text{CN})_2' \rightleftharpoons \text{Ag}' + 2\text{CN}'$, but the Ag' ion concentration is so small that it is not precipitated by chlorides as silver chloride (solubility product of $\text{AgCl} = [\text{Ag}'] \times [\text{Cl}'] = 1.2 \times 10^{-10}$), although it is precipitated as silver sulphide by alkali sulphides (solubility product of $\text{Ag}_2\text{S} = [\text{Ag}']^2 \times [\text{S}'] = 1.6 \times 10^{-49}$).

In the separation of copper and cadmium, hydrogen sulphide is passed into a solution containing $\text{Cu}(\text{CN})_4'''$ and $\text{Cd}(\text{CN})_4''$ in presence of a small excess of alkali cyanide. The cuprous ion concentration from the $\text{Cu}(\text{CN})_4'''$:

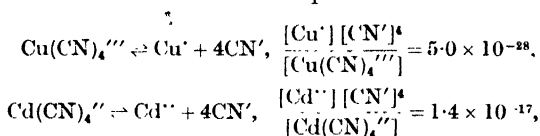


is too small to exceed the solubility product of Cu_2S , but the cadmium ion concentration from the less stable $\text{Cd}(\text{CN})_4''$:



is large enough to exceed the solubility product of CdS and this is precipitated (see the full calculation in Partington and Stratton, *Intermediate Chemical Calculations*, Chap. XI).

The dissociation constants of the complex ions are:



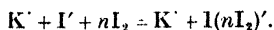
the first complex ion being much more stable than the second.

Methods used for the detection of complex ions and in some cases the determination of their formulae include:

(1) *Abnormal solubilities.*—Silver cyanide dissolves in potassium cyanide solution and the composition of saturation is approximately $\text{AgCN} : \text{KCN}$, hence the complex ion is probably $\text{Ag}(\text{CN})_2'$.

(2) *Distribution coefficient.*—Ammonia is extracted from water solution by chloroform, and from the composition of the chloroform layer and the distribution coefficient (p. 66) the NH_3 concentration in the water is found. Cupric hydroxide dissolves in ammonia to form a deep blue solution, and from the distribution ratio with chloroform the concentration of free ammonia in the solution is calculated. The remainder is combined with the copper, and thence the composition of the complex ion is calculated as $\text{Cu}(\text{NH}_3)_4''$.

(3) The *freezing-point depression* gives the total number of particles, ions and molecules, in a solution. On adding iodine to potassium iodide solution the freezing point is unchanged, hence the reaction is



Method (2) shows that $n = 1$ and the ion is I_3' . Similarly the aluminate ion is found to be AlO_2' : $Al(OH)_3 + OH' = AlO_2' + 2H_2O$.

(4) *Abnormal transport numbers* (p. 234) indicate the formation of complex anions from metal cations, e.g. in concentrated CdI_2 solution part of the cadmium travels to the *anode*, because the ion CdI_4'' is present.

(5) *Conductivity changes* indicate the increase or decrease of the number of ions in solution and sometimes the formation of complex ions can be detected.

(6) *Electromotive force* measurements will sometimes decide the formula of a complex ion $M_rA_r \rightleftharpoons qM^+ + rA^-$ by measurement of the metal ion concentration $[M^+]$ from electrode potentials (p. 799), and variation of the concentration of the solution and of the concentration of a salt with a common ion A. This method has been used with complex cyanides.

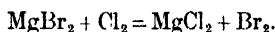
CHAPTER XX

THE HALOGENS

THE elements fluorine, chlorine, bromine, and iodine form a group called the **halogen elements** or **halogens** (from the Greek *hals*, salt). Chlorine and its compounds have been dealt with ; in the present chapter the other three halogens are described, fluorine (although it has the smallest atomic weight) last, since it differs in many ways from the other elements of the group. At the ordinary temperature fluorine and chlorine are gases, bromine a liquid, and iodine a solid.

BROMINE

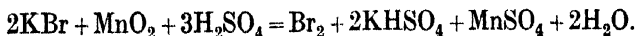
History.—Bromine was discovered by Balard in 1825 (published in 1826) in the residues from the manufacture of salt from sea water. These liquors are known as *bittern* and contain magnesium bromide $MgBr_2$. When treated with chlorine a yellow colour is produced due to liberation of free bromine :



Bromine was recognised as an element of the same character as chlorine and its discovery was further evidence in favour of the elementary nature of the latter. The free element is a dark-red heavy liquid giving a red vapour with a most irritating odour, hence its name (from the Greek, *bromos*, a stench).

Occurrence.—Bromine occurs in the rare mineral *bromargyrite* $AgBr$. Magnesium and alkali metal bromides occur in sea water, in some mineral springs, in the Dead Sea and the Great Salt Lake (Utah), and in the Stassfurt salt deposits. Most of the bromine made commercially is now obtained from sea water : average sea-water contains 0.015 per cent of bromine, but the Dead Sea and the Great Salt Lake of Utah contain considerable quantities of bromides, traces of which also occur in the Northwich brine. Bromine in combination is found in sea animals and plants ; the ancient Tyrian purple, obtained from a shell-fish, consists of a dibromo-indigo.

Preparation.—Bromine can be obtained in the laboratory by heating potassium bromide with diluted sulphuric acid and manganese dioxide in a retort :



2.5 gm. of powdered KBr , mixed with 7 gm. of MnO_2 , are distilled in a retort with 15 ml. of H_2SO_4 mixed with 90 ml. of water. The red bromine

vapour is condensed in a little water in the receiver. A red solution of bromine (*bromine water*) is formed, and a little nearly black liquid bromine settles out. The vapour acts violently on the mucous membranes, so that experiments with bromine should be carried out in a good draught. It also corrodes cork and indiarubber. The liquid should be kept in a well-stoppered bottle. It corrodes the skin, which should at once be washed with petroleum if it comes in contact with bromine. The vapour attacks the eyes powerfully and the element is poisonous.

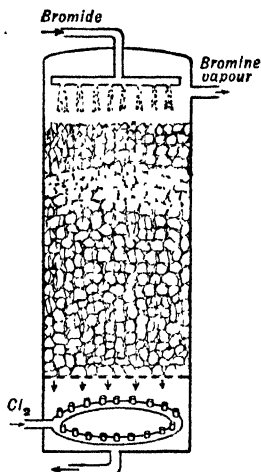
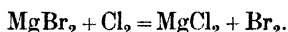


FIG. 172.—Technical preparation of bromine

Bromine is prepared technically from the Stassfurt or other bromides by passing chlorine and steam into the solution in a tower packed with pieces of porcelain (Fig. 172) :

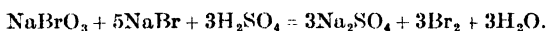


The bromine vapour is condensed by cooling and any passing on is caught by passing through moist iron filings, when a solution of iron bromide is formed, which is used in the preparation of potassium bromide (p. 323).

Bromine is extracted in America (Wilmington N.C., etc.) from sea water, which is acidified and chlorinated. The bromine vapour blown out by a current of air is absorbed in alkali and a mixture of bromate and bromide is formed :

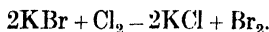


This is acidified, when bromine is liberated :

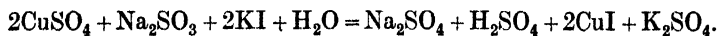


To obtain 1 lb. of bromine 1800 gallons of sea water are treated. Most of the bromine is used in making ethylene dibromide ($\text{C}_2\text{H}_4 + \text{Br}_2 = \text{C}_2\text{H}_4\text{Br}_2$) for "ethyl petrol" containing lead tetraethyl. Some is used in making dyes, in gold extraction, and in making bromides for medicinal use. Bromine is used to some extent as a disinfectant, absorbed in sticks of diatomic brick : the product (75 per cent Br_2) is called *solid bromine*.

Bromine may be purified by careful distillation. Chlorine is removed by distillation over potassium bromide :



Iodine is removed as a precipitate of cuprous iodide by adding a solution of copper sulphate and sodium sulphite to a solution of impure alkali bromide :



Sulphuric and hydrobromic acids are removed by allowing the bromine to stand over quicklime and anhydrous calcium bromide, and distilling.

Scott's preparation of pure hydrobromic acid (p. 322) is a good method of obtaining a pure bromine compound.

Properties.—Bromine is a dark red (almost black) liquid of high density (3.188 at 0° and 3.119 at 20°), which at room temperature evolves a red poisonous vapour of most irritating odour. It freezes to a dark red solid, m.pt. -7.3° ; at -252° this is orange; the boiling point is 58.80° . The vapour density at 228° corresponds with the formula Br_2 . At 1050° 6.3 per cent dissociation into atoms occurs: $\text{Br}_2 \rightleftharpoons 2\text{Br}$. The stability of the halogen molecule decreases with increasing atomic weight; F_2 is very stable, Cl_2 is 0.0025 per cent, Br_2 0.3 per cent, and I_2 2.88 per cent dissociated at 1000° abs.

Bromine combines directly with many elements forming bromides. The reactions are usually more vigorous than those between the same elements and chlorine *gas*, but the bromine is in the *liquid* state, *i.e.* more highly concentrated.

Five ml. of bromine are poured into a test-glass standing inside a bell-jar over a draught-hole in the bench. The top of the jar is closed by a glass plate. A *small* piece of white phosphorus thrown into the liquid causes an explosion and is projected from the liquid. Red phosphorus burns quietly with a dull red flame forming yellow fumes of the pentabromide PBr_5 . Powdered arsenic burns with a reddish-white flame, forming fumes of AsBr_3 . A *small* piece of potassium combines explosively forming KBr . Sodium does not combine with bromine unless heated to 200° in the vapour, or when water is added.

Bromine vapour bleaches moist litmus paper, but more slowly than chlorine. Starch-paste is coloured orange-yellow by bromine. In water, 3.6 parts of bromine dissolve in 100 at 20° : the solubility decreases with rise of temperature. The red solution loses bromine on exposure to air. The freezing point shows that the bromine molecule in solution is Br_2 . Bromine water is stable in the dark but decomposes in bright sunlight: $2\text{Br}_2 + 2\text{H}_2\text{O} = 4\text{HBr} + \text{O}_2$. If saturated bromine water is cooled in a freezing mixture in presence of bromine, red solid bromine hydrate $\text{Br}_2 \cdot 8\text{H}_2\text{O}$ separates. This decomposes at 6.2° into bromine water and bromine.

Chloroform, benzene, and carbon disulphide extract bromine from its solution in water, forming orange-red liquids.

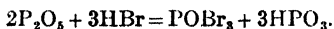
Add a little chlorine water to a solution of KBr and shake with chloroform. The latter separates, containing most of the bromine as a red solution. Shake this with sodium hydroxide solution. The chloroform becomes colourless and the aqueous layer contains sodium bromide and hypobromite:



Hydrogen bromide.—Bromine vapour combines with hydrogen when the mixture is passed over heated platinum: $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$. The combination is not attended with explosion (as in the case of hydrogen and chlorine) and does not begin in the absence of a catalyst, even in bright sunlight, below 300° . In presence of platinum, combination

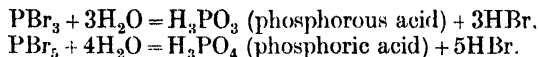
begins at 200°. The heat of formation of HBr from gaseous Br₂ is only 11 k. cal. per gm. mol. as compared with 22 k. cal. with HCl.

Pure dry hydrogen is passed slowly through dry bromine in a bubbler, at 35°–40°, when a mixture of hydrogen and bromine vapour is formed. This is passed through a hard glass tube containing platinised asbestos. When the air is displaced, the tube is heated to about 200°, when reaction proceeds, usually without further heating. To remove unconverted bromine vapour (present only when a rapid stream of gas is used) the gas is passed through a tube packed with solid ferrous bromide, and it is then passed through one or more tubes containing fused calcium bromide in order to dry it. If pure hydrogen bromide is required the gas is condensed by cooling in liquid air, when the excess of hydrogen passes on and solid hydrogen bromide is obtained. This process (a modification of that used by Baxter, 1931) is superior to the use of an electrically heated platinum spiral. Phosphorus pentoxide reacts *slowly* with hydrogen bromide, some POBr₃ being formed :



Calcium chloride is a satisfactory drying agent for most purposes.

Hydrogen bromide is usually prepared by dropping bromine on a mixture of red phosphorus and water. Phosphorus tribromide and pentabromide are probably first formed, and at once decomposed by water :



Twenty gm. of red phosphorus and 40 ml. of water are placed in a flask, and 40 ml. of bromine are added *drop by drop* from a tap funnel (Fig. 173).

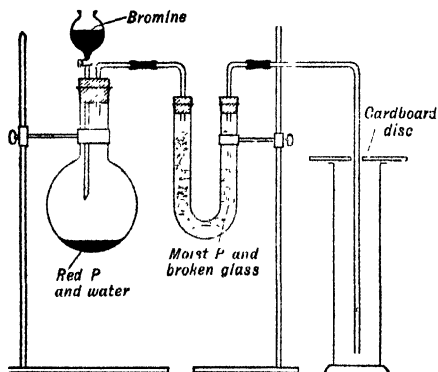


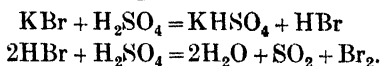
FIG. 173.—Preparation of hydrogen bromide.

The gas is passed through a U-tube loosely filled with broken glass smeared with moist red phosphorus. This removes unchanged bromine vapour. The addition of the first few drops of bromine is attended by lambent green flames, but when the air is displaced these are not formed. At the end of the reaction the flask is gently heated. The gas is collected by downward displacement in a dry jar covered with a perforated glass plate or cardboard

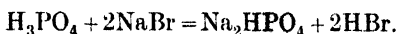
disc. It may be collected over mercury: The gas fumes strongly in moist air and (like HCl and HI) has an irritating acid smell.

Hydrogen bromide may be obtained by the action of bromine on benzene in presence of aluminium: $C_6H_6 + 2Br_2 = C_6H_4Br_2$ (dibromobenzene) + $2HBr$.

The method of heating a salt with concentrated sulphuric acid which was used for the preparation of hydrochloric acid is not suitable for the preparation of hydrobromic acid. This is first liberated but (unlike hydrochloric acid) it can act as a reducing agent. It reduces the hot concentrated sulphuric acid to sulphur dioxide and the hydrobromic acid evolved is mixed with sulphur dioxide and bromine vapour:



When syrupy phosphoric acid is heated with the bromide, however, only hydrobromic acid is evolved:



The physical properties of hydrogen bromide are as follows:

Melting point	- 86.9°.	Normal density	3.644 gm. per lit.
Boiling point	- 66.7°.	Density of liquid at b. pt.	2.160.
Critical temperature	+ 89.8°.		

Hydrogen bromide is decomposed when passed over heated platinum and a state of equilibrium is set up: $2HBr \rightleftharpoons H_2 + Br_2$. An excess of hydrogen is used in preparing hydrogen bromide (see above), when combination is nearly complete.

The thermal dissociation of hydrogen bromide is given below, in percentages. The dissociation of hydrogen bromide by heat is greater than that of hydrogen chloride but less than that of hydrogen iodide.

t° C.	-	-	-	727	1108	1220
per cent decomp. of HBr	-	-	-	0.18	0.84	1.15

The composition of hydrogen bromide may be demonstrated by the action of sodium amalgam on the gas, as with hydrogen chloride (p. 212). Half the volume of hydrogen remains, hence the hydrogen bromide molecule contains half a molecule or one atom of hydrogen and the formula is $HBr_{\frac{1}{2}}$. The density shows that the molecular weight is 81, hence one atom of bromine ($Br = 80$) is present and the formula is HBr .

Hydrogen bromide is very soluble in water; 1 vol. of water dissolves 600 vols. of the gas at 0°. The solution is a strong acid: $HBr \rightleftharpoons H^+ + Br^-$. Concentrated hydrobromic acid fumes in moist air. On distillation it forms an acid of maximum boiling point, the composition varying with the pressure; it is not a definite hydrate. The boiling point under 760 mm. is 126° (47.5 per cent HBr), under 1952 mm. it is 153° (46.3 per cent HBr). The solution saturated at 0° contains 69, that at 25°, 66 per cent of HBr.

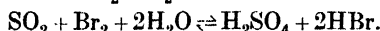
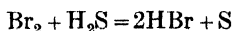
If 0.2 gm. of stannous chloride and 3.4 ml. of sulphuric acid are added to 25 ml. of a solution of 15 gm. of KBr and the mixture distilled, a solution of hydrobromic acid free from bromine is obtained.

Aqueous hydrobromic acid may be prepared by passing the gas into water through an inverted retort, as shown in Fig. 174. If liquid is driven back, it collects in the bulb of the retort.

A solution of the acid is also prepared by passing hydrogen sulphide or sulphur dioxide into bromine covered with a layer of water. The second method gives almost pure hydrobromic acid (Scott, 1900).



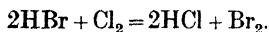
FIG. 174.—Preparation of aqueous hydrobromic acid.



Three hundred and fifty ml. of bromine are covered with 2 litres of water in a flask, and a current of SO_2 from a siphon of liquid passed into the water, through a tube ending just above the surface of the bromine, until the whole is converted into a pale-yellow homogeneous liquid, which is distilled. The liquid is redistilled over BaBr_2 to remove sulphuric acid carried over in the first distillation.

The solid hydrates $\text{HBr}\cdot 2\text{H}_2\text{O}$, m. pt. $-11\cdot 2^\circ$, $\text{HBr}\cdot 3\text{H}_2\text{O}$, m. pt. $-47\cdot 5^\circ$, and $\text{HBr}\cdot 4\text{H}_2\text{O}$, m. pt. $-55\cdot 8^\circ$, are formed on cooling very concentrated solutions.

Aqueous hydrobromic acid is slowly decomposed by oxygen in sunlight, becoming yellow from liberation of bromine: $4\text{HBr} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Br}_2$. A mixture of dry hydrogen bromide gas and oxygen is not decomposed on exposure to light. The gas or solution is decomposed by chlorine:

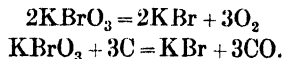


Bromides.—Hydrobromic acid solution dissolves zinc, iron, and many other metals (copper in a hot concentrated solution) with evolution of hydrogen, forming bromides, which may also be obtained by neutralising the acid with oxides, hydroxides, or carbonates, and by the direct union of metals with bromine.

The alkali bromides are obtained by dissolving bromine in a solution of alkali:

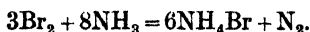


evaporating, and heating strongly to decompose the bromate. The residue on evaporation may be mixed with powdered charcoal and heated, when the bromate is reduced at a lower temperature:

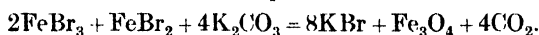


The mass is warmed with water, filtered from excess of charcoal, and crystallised by evaporation.

Ammonium bromide free from bromate is obtained by the action of bromine on cooled ammonia solution:



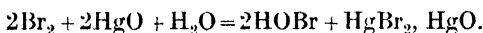
In the manufacture of bromine, a solution of ferrous and ferric bromides is obtained (p. 318). When this is mixed with a solution of potassium carbonate, a precipitate of hydrated ferrosiferrous oxide (which is easily filtered) and a solution of potassium bromide are formed :



Nearly all bromides are soluble in water, but silver, lead, cuprous, and mercurous bromides only very sparingly. Silver nitrate solution gives a yellowish-white precipitate of AgBr , insoluble in dilute nitric acid and sparingly soluble in dilute ammonia (*cf.* AgCl and AgI). Palladium nitrate gives a reddish-brown precipitate of palladous bromide PdBr_2 . The formation of free bromine, soluble in chloroform with a red colour, by the action of chlorine water, and the formation of red bromine vapour when the substance is heated with MnO_2 and H_2SO_4 , are also characteristic reactions.

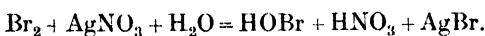
Oxides of bromine.— Br_2O is said to be formed in small amounts by passing bromine vapour over precipitated mercuric oxide (*cf.* Cl_2O). An oxide Br_3O_8 is formed as a white crystalline solid by the action of pure (100 per cent) ozone on purified bromine vapour at -5° to $+10^\circ$ under low pressure (Schumacher and Lewis, 1929). It exists in two modifications with a transition point at -35° . The oxide Br_3O_8 is stable at -80° , but unless the materials for its preparation are very pure and the apparatus very clean, an explosion results. Another oxide BrO_2 is said to be formed as a yellow solid, stable below 0° , by the action of an electric discharge on a mixture of bromine vapour and excess of oxygen in a strongly cooled tube (Schwarz and Schumacher, 1937).

Hypobromous acid.—By shaking bromine water with precipitated mercuric oxide a solution of hypobromous acid and an insoluble oxybromide of mercury are formed :



By adding more bromine and mercuric oxide, a solution containing 6 per cent of HOBr may be obtained, which may be distilled in a vacuum at 40° . It is a straw-yellow liquid, decomposing when heated with production of bromine and bromic acid, and is a powerful oxidising and bleaching agent.

A solution of hypobromous acid is formed by the action of bromine on concentrated silver nitrate solution and distillation :



If bromine is dissolved in excess of cold alkali hydroxide solution, an unstable hypobromite is formed : $\text{Br}_2 + 2\text{NaOH} = \text{NaBr} + \text{NaOBr} + \text{H}_2\text{O}$. These are used as oxidising agents and in the estimation of hydrogen peroxide and of urea. On keeping, the solutions decompose with formation of bromide and bromate : $3\text{NaOBr} = 2\text{NaBr} + \text{NaBrO}_3$. Bromine vapour is absorbed by dry slaked lime, forming a red powder similar to bleaching powder. This, when distilled with dilute nitric acid, gives a solution of hypobromous acid.

Bromous acid HBrO_2 is unknown, but bromites are formed in solution by the spontaneous decomposition of hypobromites : $2\text{BrO}' = \text{BrO}_2' + \text{Br}'$.

They rapidly decompose: $3\text{BrO}_2' = 2\text{BrO}_3' + \text{Br}'$. Bromites only slowly decompose urea, ammonia, or phenol (distinction from hypobromites), but oxidise arsenites to arsenates (distinction from bromates).

Bromic acid.—When bromine in slight excess is dissolved in hot concentrated alkali hydroxide solution, a bromate and bromide are formed:



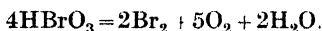
Potassium bromate is much less soluble than the bromide and separates in crystals on cooling, as in the case of the chlorate. Potassium bromate also separates when bromine vapour is passed into a solution of potassium carbonate which has been saturated with chlorine: $6\text{KOC}l + \text{Br}_2 = 2\text{KBrO}_3 + 4\text{KCl} + \text{Cl}_2$.

Potassium bromate is formed by passing chlorine into an alkaline bromide solution: $\text{KBr} + 6\text{KOH} + 3\text{Cl}_2 = \text{KBrO}_3 + 6\text{KCl} + 3\text{H}_2\text{O}$.

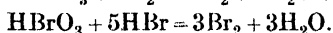
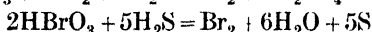
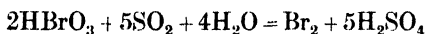
When silver nitrate is added to a solution of potassium bromate white silver bromate AgBrO_3 is precipitated. When this is shaken with bromine water, insoluble silver bromide is formed and the filtered solution contains bromic acid:



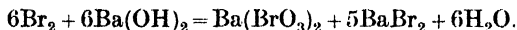
By evaporation on a water-bath a 5 per cent solution, and by concentration in a vacuum desiccator a colourless 50 per cent solution, may be obtained, but more concentrated solutions evolve bromine and oxygen:



Bromic acid is a powerful oxidising agent:



Barium bromate $\text{Ba}(\text{BrO}_3)_2$ is precipitated when bromine is added in slight excess to hot concentrated baryta water:



The bromide is soluble and remains in solution. If barium bromate is digested with dilute sulphuric acid, and the excess removed by baryta water, the filtered solution contains bromic acid.

Bromates are usually sparingly soluble. On heating they decompose; perbromates are not formed and are not known:

1. KBrO_3 , $\text{Hg}_2(\text{BrO}_3)_2$, and AgBrO_3 , give bromide + oxygen,
2. $\text{Mg}(\text{BrO}_3)_2$, $\text{Zn}(\text{BrO}_3)_2$, $\text{Al}(\text{BrO}_3)_3$, give oxide + bromine + oxygen;
3. $\text{Pb}(\text{BrO}_3)_2$ and $\text{Cu}(\text{BrO}_3)_2$ give oxide and bromide.

A mixture of $\text{NaBrO}_3 + 5\text{NaBr}$ is prepared by saturating concentrated sodium hydroxide solution with bromine, and draining the separated crystals. To these sufficient NaBrO_2 , prepared by electrolytic oxidation of NaBr , is added to form $\text{NaBrO}_3 + 2\text{NaBr}$, and the mixture is used under the name of *bromine salt* in the extraction of gold.

Bromine chloride.—Chlorine merely dissolves in liquid bromine and no compound has been obtained in the pure state, although BrCl appears from spectroscopic evidence to exist to some extent in a mixture of chlorine and bromine vapour.

IODINE

History.—Iodine was discovered by Courtois in 1811 in the mother liquor from the manufacture of soda from kelp (burnt seaweed), but was first carefully investigated by Davy and by Gay-Lussac in 1813. They recognised that it was an element similar to chlorine. It was called iodine from the violet colour of the vapour (Greek, *ioeides*, violet).

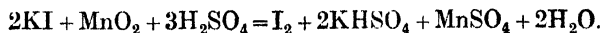
Occurrence.—Iodides occur rather rarely as *iodargyrite* (silver iodide), in some magnesian limestones and dolomites, and in some lead ores. Iodides occur in some mineral waters (Woodhall Spa near Lincoln, Montpellier, Heilbrunn). (Free iodine is said to exist in the water of Woodhall Spa.) The salt brine from petroleum wells in Java contains about 1.35 gm. per litre of iodine as iodides. This is precipitated as cuprous iodide (p. 318), from which iodine is extracted. In California, a similar but weaker brine is worked for iodine. The iodine content of sea-water exists partly as organic compounds and partly as iodides or iodates: it never exceeds 0.001 per cent and in the Atlantic is only 1 part in 280 millions. Seaweeds and sponges absorb this iodine, partly in the form of organic compounds.

Tropical sponges may contain as much as 10 per cent of iodine, whilst Turkey sponges contain about 0.2 per cent. The amount of iodine is greater in deep-sea weeds than in those growing near the shore. During storms, these weeds are torn up and cast ashore. They are known in Scotland as *drift-weeds*, or *red wracks*; the varieties *Laminaria digitata* and *L. stenophylla* alone are used in the preparation of iodine.

Iodine occurs in oysters and many sea-animals. It is present in traces in cod-liver oil as an organic compound, and occurs as an organic compound thyroxine $C_{15}H_{11}O_4NI_4$ in the thyroid gland (those of the ray and dogfish contain 1 per cent of iodine).

Another source of iodine is the alkali iodate (perhaps also some periodate) contained up to 0.2 per cent as $NaIO_3$ in crude Chile nitre (*caliche*). The mother-liquors from the crystallisation of the sodium nitrate contain about 3 gm. of iodine as iodate per litre.

Preparation.—In the laboratory, iodine may be obtained by heating potassium or sodium iodide with diluted sulphuric acid and manganese dioxide:



Heat 3.5 gm. of KI with 7 gm. of MnO_2 and 100 ml. of dilute H_2SO_4 (1:6) in a retort. The violet vapour condenses in the neck of the retort and in the receiver as glittering black scales of solid iodine.

In making iodine from sea-weed two processes are used.

In one the weeds are burnt in shallow pits and the ash called *kelp* (*varec* in Normandy) contains potassium salts and from 0.4 to 1.3 per cent of

iodine as iodides. Formerly in Normandy, Spain, and Scotland the ash was used in the manufacture of potash; the technical preparation of iodine was begun by Dr. Ure at Glasgow and is also carried out in Norway and Japan. The kelp is lixiviated with water in iron vats heated by steam and the solution concentrated in iron pans. The alkali carbonates, chlorides and sulphates crystallise and the final mother-liquor contains the very soluble sodium and potassium iodides, with some bromides. It is mixed with sulphuric acid, and the sulphur (from the decomposition of sulphides) allowed to settle. The clear liquor is run into iodine stills, consisting of iron pots with dome-shaped lead covers communicating with trains of earthenware receivers called *udells* or *aludels* (Fig. 175). Manganese dioxide is added

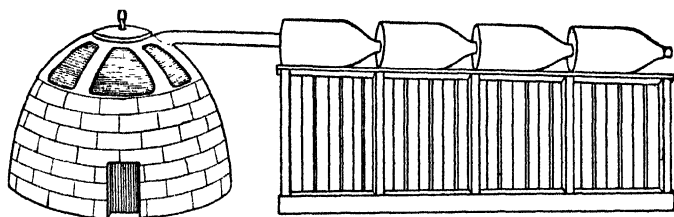
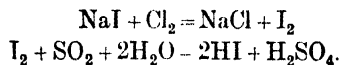


FIG. 175.—The technical preparation of iodine.

and iodine distils on heating, collecting in the *udells*. It is purified by sublimation in porcelain pans. About 12 lb. of iodine are obtained per ton of kelp, representing about half that contained in the original seaweed.

In the second process, used in Norway, a wet extraction of the weed with sodium carbonate solution is used, and an organic adhesive is precipitated on acidifying of the solution.

In extracting iodine from the California salt-brine, this is chlorinated and the iodine blown out as vapour in a current of air. The iodine vapour is absorbed in a solution of hydrogen iodide and sulphuric acid, which is circulated in absorbers. The free iodine in the solution is continuously reduced by adding sulphur dioxide :



Part of the solution is continuously withdrawn from circulation and the iodine precipitated from it by chlorine, filtered, melted under concentrated sulphuric acid and cast into blocks. It is sufficiently pure for chemical purposes, but for pharmaceutical uses it is purified by sublimation.

The iodide in the clarified brine may also be precipitated as silver iodide, which is decomposed by iron into silver and ferrous iodide. Silver iodide is precipitated before the bromide or chloride.

The preparation of iodine from the iodate in Chile nitre (*caliche*) involves reduction.

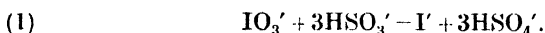
The mother-liquor ("aqua vieja") is run into a wooden vat and sodium hydrogen sulphite solution added. The iodine precipitated is pressed and sublimed.

The reaction has been variously represented; it involves the

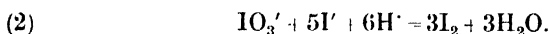
reduction of iodate to iodine and the oxidation of the sulphite to sulphate, *e.g.* by the reaction :



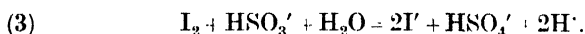
which occurs in stages. The iodate is reduced to iodide by a rather slow reaction :



The iodide reacts rapidly with iodate to form iodine :



As long as any sulphite remains, the iodine is reduced to iodide by a very rapid reaction :



Iodine appears only when all the free sulphurous acid is used up, and the process shows a *period of induction*. This is shown in the following experiment, due to Landolt.

Dissolve 10 gm. of crystallised iodic acid in 1 litre of water. Saturate 5 ml. of water with sulphur dioxide, and add to 1 litre of water. 50 ml. of iodic acid solution are added to 250 ml. of water and a little starch solution in a cylinder. 50 ml. of the sulphurous acid are diluted with 250 ml. of water and the solution poured into the iodic acid. The liquid remains colourless for a certain interval, and then at once becomes blue. By varying the dilution, the time interval may be altered.

Pure iodine.—Commercial iodine nearly always contains iodine chloride ICl, iodine bromide IBr, and sometimes cyanogen iodide ICN, all of which are volatile and cannot be separated by sublimation. Resublimation over potassium iodide removes most of the impurity.

Iodine is ground in a mortar with potassium iodide and the mixture gently heated in a porcelain dish on a sand-bath. A larger porcelain dish filled with cold water is placed over the first and the purified iodine condenses on its under surface in glittering scales.

Stas dissolved resublimed iodine in concentrated potassium iodide solution, precipitated it with water, and distilled in steam. The solid iodine was collected, dried *in vacuo* over solid calcium nitrate (frequently renewed), and finally sublimed over barium oxide BaO, to separate HI and H₂O. Lean and Whatmough (1900) heated pure cuprous iodide at 240° in a current of dry air :



Baxter heated pure iodine pentoxide, from recrystallised iodic acid, at 300° in a platinum boat in a quartz tube : $2\text{I}_2\text{O}_5 = 2\text{I}_2 + 5\text{O}_2$.

Properties of iodine.—Iodine is a blackish-grey opaque crystalline solid which has almost a metallic lustre. (When deposited in thin films on glass at -180° it is transparent.) Large rhombic crystals (Fig. 176) are produced by spontaneous evaporation of an ether solution, or by allowing concentrated hydriodic acid to oxidise by exposure to air.

The physical properties are: density at 18°, 4.94; m.pt. 113.9°; b. pt. 184.4°. Although the vapour pressure at room temperature is small (0.13 mm. at 15°, 0.47 mm. at 20°), iodine has a characteristic smell and in a closed flask the vapour shows a faint colour.

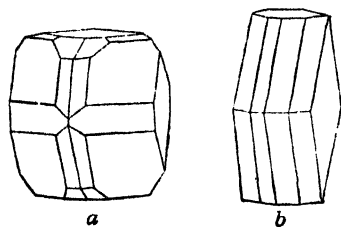


FIG. 176.— Iodine crystals.

Iodine vapour when pure has a splendid deep-blue colour: when mixed with air it is reddish-violet (Stas). The vapour density decreases with rise of temperature. From the boiling point to 700° it corresponds with the formula I_2 ; the density then diminishes to 1700°, when according to Victor Meyer it again becomes constant and corresponds with the formula I . The dissociation into atoms: $I_2 \rightleftharpoons 2I$ is well established with iodine. Starek and Bodenstern (1910) give 45 per cent dissociation at 1200° and extrapolation indicates complete dissociation only at about 3000°. Iodine vapour shows an orange-yellow fluorescence, especially when exposed to green light. When exposed to light from a mercury lamp it emits a spectrum consisting of a large number of equally-spaced lines.

Iodine is much less soluble in water than either chlorine or bromine; 0.2765 gm. per litre at 18°, 0.4662 at 35°, and 0.9226 at 55°. The solution is brownish-yellow. Iodine is readily soluble in solutions of hydriodic acid or iodides, forming dark-brown liquids containing the ion I_3^- . From a solution in potassium iodide black crystals of potassium tri-iodide $KI_3 \cdot H_2O$ separate. Many other polyiodides are known. Iodine is readily soluble in alcohol forming brown *tincture of iodine* ($\frac{1}{2}$ oz. each of iodine, potassium iodide and water, and rectified spirit to 1 pint).

Solutions of iodine in carbon disulphide are violet, the same colour as the vapour. In benzene and chloroform reddish-purple solutions are formed. In these solutions mainly I_2 molecules are present. The depression of freezing point of methylene iodide CH_2I_2 containing iodine gives the formula I_2 . The purple solutions in petrol ether show colloidal particles in a beam of light, and these are formed in solutions in toluene on exposure to light. The solution in petrol ether (but not that in carbon disulphide) becomes brown on cooling in solid carbon dioxide and ether.

In water, alcohol, ether, and potassium iodide solution, iodine forms brown solutions. A purple solution in chloroform becomes brown on addition of alcohol, but the original colour is restored on dissolving out the alcohol by shaking with water. The brown solution in alcohol contains associations of iodine with solvent molecules.

Iodine combines directly with many elements forming iodides. It explodes when heated with potassium but can be fused with sodium without reaction (cf. Br_2). Powdered antimony inflames in the vapour, solid iodine inflames white phosphorus, and when ground in a mortar

with mercury it forms green mercurous iodide or yellow mercuric iodide according to the proportions used.

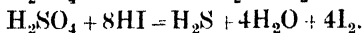
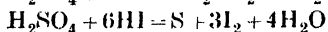
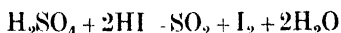
Test for iodine.—Solutions of iodine give a beautiful blue colour with starch-paste, prepared by warming "soluble starch" with water or adding boiling water to ordinary starch made into a paste with cold water. 1 part of iodine in 5,000,000 parts of water may be detected. The blue colour disappears on heating but reappears on cooling.

Add a drop of a solution of iodine in potassium iodide to some dilute potato starch solution in a test-tube. Heat the tube in a beaker of boiling water: the blue liquid becomes colourless. Cool the lower part of the tube in a beaker of cold water: this part of the liquid again becomes blue. If excess of chlorine water is added, the blue colour disappears, since iodine chloride ICl is formed.

The blue substance has been variously described as a chemical compound ("iodide of starch"), or a solid solution, or an adsorption complex of starch and iodine. A blue colour is produced by iodine with a few other substances *e.g.* saponarin, some of which are crystalline, and it is fully developed only in the presence of iodides or electrolytes. Basic lanthanum and praseodymium acetates (which are colloidal) and moist potassium acetate also give a blue colour with iodine, but the reaction is very specific.

Hydrogen iodide.—Hydrogen and iodine combine only feebly: the affinity for hydrogen diminishes rapidly in the series of halogens F, Cl, Br, I. A mixture of iodine vapour and hydrogen passed over heated platinum forms gaseous hydrogen iodide giving fumes in moist air, but the reaction is reversible and incomplete: $H_2 + I_2 \rightleftharpoons 2HI$.

Hydrogen iodide is evolved on heating potassium iodide with phosphoric acid; with sulphuric acid oxidation occurs, iodine is set free and some of the sulphuric acid reduced. Since hydrogen iodide is a more powerful reducing agent than hydrogen bromide, the sulphuric acid is reduced not only to sulphur dioxide but also to sulphur and hydrogen sulphide:



The usual method of preparation of hydrogen iodide gas is by the action of water on a mixture of red phosphorus and iodine:

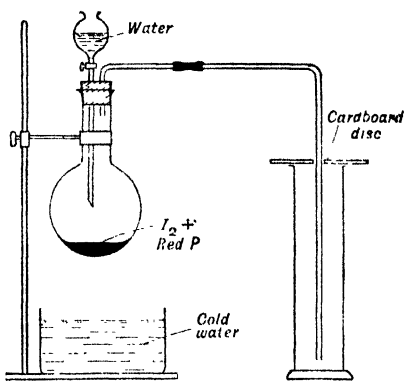
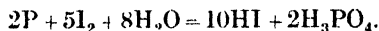


FIG. 177.—Preparation of hydrogen iodide.

Phosphorus iodide may be formed and then decomposed by water (cf. the preparation of hydrobromic acid), but it should be noted that PI_5 is not known.

Four gm. of red phosphorus and 20 gm. of iodine are shaken together in a flask, and about 15 ml. of water slowly dropped on from a tap-funnel. The evolution of gas may become very rapid, and the flask is then cooled. The gas is collected by displacement (Fig. 177). It may be dried with $CaCl_2$. It is very soluble in water and attacks mercury.

Hydrogen iodide is evolved on heating a mixture of iodine with colophonium resin.

Hydrogen iodide is a colourless gas, very soluble in water (425 vols. HI in 1 vol. at 10°) and fuming strongly in moist air. It condenses to a liquid under 4 atm. pressure at 0° , and is more easily liquefied than HCl or HBr. The physical properties of HI are as follows:

Boiling point - 35.4° .	Critical pressure 81 atm.
Melting point - 50.8° .	Normal density 5.7888 gm. per lit.
Critical temperature 150° .	

The volumetric composition of the gas may be demonstrated by the action of sodium amalgam, as in the case of hydrogen chloride and bromide. Half the volume of hydrogen remains, hence the formula is HI_x . The density gives the molecular weight 128, and the atomic weight of iodine is 127, hence $x=1$ and the formula is HI.

Dry hydrogen iodide mixed with dry oxygen is decomposed on exposure to light with liberation of iodine: $4HI + O_2 = 2H_2O + 2I_2$. According to Berthelot, a mixture of 4 vols. of HI and 1 vol. of O_2 burns with a red flame when kindled, and a jet of hydrogen iodide burns, emitting violet fumes of iodine, when surrounded by oxygen, as in the combustion of ammonia (p. 517). A red flame and violet fumes of iodine are formed when warm fuming nitric acid is poured into a jar of hydrogen iodide gas.

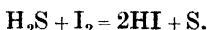
Hydrogen iodide is decomposed by exposure to sunlight: after ten days Victor Meyer found 60 per cent decomposed; after a year, 99 per cent. This photochemical decomposition occurs according to the primary reaction: $HI = H + I$. The gas is decomposed by heat: $2HI \rightleftharpoons H_2 + I_2$: decomposition begins at 180° , but is very slow. The rate of decomposition is quicker the higher the temperature. At each temperature a state of equilibrium is attained, the same from the mixture of hydrogen and iodine vapour ($H_2 + I_2$) as from hydrogen iodide ($2HI$): $2HI \rightleftharpoons H_2 + I_2$. A catalyst (e.g. platinum) produces no change in composition of the equilibrium mixture, since it accelerates equally both the direct and reverse reactions. The equilibrium percentage dissociations of HI (Bodenstein) are:

$t^\circ C.$	-	-	-	-	283°	356°	444°	527°	1022°
per cent dissociation	-	-	-	-	17.9	19.5	22.0	24.7	32.9

A solution of hydriodic acid is formed by dissolving the gas in water. The apparatus shown in Fig. 174 may be used. The solution saturated at 0° has a density of 1.99 and contains 90 per cent of HI. The hydrates

HI, 2H₂O, m. pt. - 43°, HI, 3H₂O, m. pt. - 48°, and HI, 4H₂O, m. pt. - 36·5°, separate on cooling. The solution of density 1·5 is used in organic chemistry as a reducing agent. An acid of maximum boiling point 126° at 76 cm. contains 57 per cent of HI. The freshly-prepared solution is colourless, but rapidly becomes brown when exposed to air owing to formation of iodine which dissolves in the acid: $4\text{HI} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{I}_2$. The concentrated acid may be freed from iodine by distillation over a little red phosphorus.

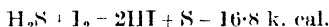
A solution of hydriodic acid is formed by passing hydrogen sulphide into a suspension of iodine in water:



When the liquid is decolourised it is saturated with iodine, and the reaction continued. When the density of the solution reaches 1·56, action ceases.

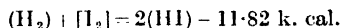
The solution is filtered from the sulphur and distilled. At first very weak acid (with hydrogen sulphide and sulphur) comes over. The temperature then rises to 126° and the 57 per cent maximum boiling-point acid distils.

Hydrogen sulphide gas reacts incompletely with dry iodine, the reaction being endothermic and reversible:

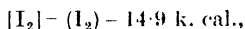


The heat of solution of (HI) in a large quantity of water is 19·2 k. cal., hence heat is evolved by the action of hydrogen sulphide on iodine in presence of water.

The formation of hydrogen iodide from hydrogen and *solid* iodine is attended by a small absorption of heat:



The heat of sublimation of iodine is



hence the reaction between hydrogen and iodine *vapour* is attended by a small evolution of heat 14·9 - 11·82 = 3·08 k. cal.

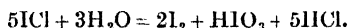


Le Chatelier's principle (p. 295) thus shows that the degree of dissociation of hydrogen iodide will increase with rise of temperature.

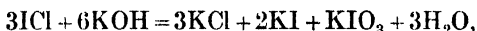
Iodides.—Iodides may be prepared by the same general methods as bromides (p. 322). Nearly all are soluble in water, cuprous, mercuric, lead, and silver iodides being exceptions. Silver iodide forms a light-yellow precipitate, insoluble in dilute nitric acid and in ammonia. The formation of violet iodine vapour when an iodide is heated with concentrated sulphuric acid and manganese dioxide, or a brown colour after addition of chlorine water, extracted by shaking with chloroform or carbon disulphide as a violet solution, may be used as tests for iodides.

Chlorides of iodine.—Iodine monochloride ICl is formed by passing chlorine over iodine, as a dark red liquid, which solidifies on standing (especially in contact with a trace of ICl_3) to a black solid: $\text{I}_2 + \text{Cl}_2 = 2\text{ICl}$. The first product of solidification melts at 14° , but is unstable and is converted on standing into a stable form melting at 27.2° , which forms red needles. This is stable under *all* conditions; from liquid cooled below 14° crystals of either form separate according as a crystal of one or the other form is added. The unstable form is obtained by cooling the liquid to -10° .

Iodine monochloride is also formed by heating iodine with potassium chlorate or boiling iodine with aqua regia. It boils at 101.3° and the vapour density is normal. It dissolves unchanged in concentrated hydrochloric acid but is somewhat decomposed by water:



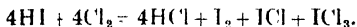
Iodine monochloride is decomposed by alkali hydroxide solution, the final reaction with excess of alkali being:



but some iodine is liberated in an intermediate stage.

Iodine trichloride ICl_3 is obtained by the action of excess of chlorine on iodine or on the monochloride: $\text{ICl} + \text{Cl}_2 \rightleftharpoons \text{ICl}_3$. The reaction is reversible, since the vapour density of the trichloride shows that it is completely dissociated at 67° . It may be fused in chlorine under 16 atm. pressure. The trichloride is also formed on heating iodine pentoxide in hydrogen chloride: $\text{I}_2\text{O}_5 + 10\text{HCl} = 2\text{ICl}_3 + 5\text{H}_2\text{O} + 2\text{Cl}_2$. It is a lemon-yellow crystalline solid.

If a jar of hydrogen iodide is inverted over a jar of chlorine there is a violent reaction, often attended by a red flame, and three substances are formed: (i) a violet vapour, depositing solid crystals of iodine; (ii) dark red drops of liquid at the junction of the two jars—iodine monochloride ICl ; (iii) lemon-yellow crystals in the lower jar—iodine trichloride ICl_3 . The reaction is:

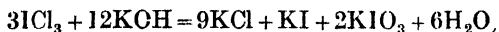


On standing in presence of excess of chlorine only yellow crystals of ICl_2 remain.

Iodine trichloride is almost completely hydrolysed by water:



and is decomposed by alkali hydroxide solution:



some iodine being liberated in an intermediate stage.

Iodine monochloride and trichloride are sometimes regarded as salts of the univalent and trivalent iodine cations, I^+Cl^- and $\text{I}^{3+}\text{Cl}_3^-$. Some salts of trivalent iodine are described: iodine acetate $\text{I}(\text{C}_2\text{H}_3\text{O}_2)_3$ is obtained by the action of Cl_2O on iodine dissolved in glacial acetic acid, and iodine perchlorate $\text{I}(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ is obtained in yellowish-green needles by the action of ozone on a cooled solution of iodine in anhydrous perchloric

acid : $I_2 + 6HClO_4 + O_3 = 2I(ClO_4)_2 + 3H_2O$; iodine orthophosphate IPO_4 is said to be formed from iodine, orthophosphoric acid, acetic anhydride and fuming nitric acid. The strongly basic diphenyliodonium hydroxide $(C_6H_5)_2IOH$ is stable and forms salts resembling those of tervalent thallium, even to giving a green flame reaction.

Iodine monobromide IBr is formed by direct combination as black crystals similar to iodine, m. pt. 36° , b. pt. 116° . The vapour is dissociated.

Oxides and oxy-acids of iodine.—The following oxygen compounds of iodine are known :

OXIDES	OXY-ACIDS
—	Hypo-iodous acid HOI
Iodine dioxide IO_2 or I_2O_4	—
The oxide I_4O_9	—
Iodine pentoxide I_2O_5	Iodic acid HIO_3
	{ Metaperiodic acid HIO_4
	{ Dimesoperiodic acid $H_4I_2O_9$
	{ Paraperiodic acid H_5IO_6

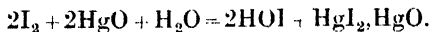
The yellow non-deliquescent iodine dioxide I_2O_4 is obtained by heating iodic acid with hot concentrated sulphuric acid till fumes of iodine are evolved, cooling and decomposing the resulting basic sulphate of iodine with water, in which iodine dioxide is sparingly soluble. It is decomposed on heating : $5I_2O_4 = 4I_2O_5 + I_2$.

The pale-yellow deliquescent oxide I_4O_9 is obtained by the action of ozonised oxygen on dry iodine. It is decomposed on heating : $4I_4O_9 = 6I_2O_5 + 2I_2 + 3O_2$, and by water : $5I_4O_9 + 9H_2O = I_2 + 18HIO_3$.

Iodine pentoxide (*iodic anhydride*) I_2O_5 is obtained by heating iodic acid at 200° , or at 150° for three hours and then at 240° in a current of dry air : $2HIO_3 = I_2O_5 + H_2O$. It is a white powder, decomposing at 300° after fusion into oxygen and iodine. When warm it oxidises carbon monoxide, even in traces in gaseous mixtures : $5CO + I_2O_5 = 5CO_2 + I_2$. The carbon dioxide formed may be absorbed by baryta water, and the amount determined by titration. Iodine pentoxide dissolves in water, forming iodic acid HIO_3 .

Hypo-iodous acid.—Iodine dissolves in cold dilute alkali hydroxide solution to form a yellow solution, with a characteristic smell of saffron. This contains hypo-iodite and iodide ; $I_2 + 2OH' = OI' + I' + H_2O$. The freshly-prepared solution has oxidising and bleaching properties. Indigo solution is bleached, hydrogen peroxide evolves oxygen, manganous sulphate is precipitated as brown manganic hydroxide, and alcohol gives a yellow precipitate of iodoform CHI_3 . An acid, even carbonic acid (soda-water), liberates iodine from the solution : $OI' + I' + 2H' = I_2 + H_2O$.

On standing, especially if heated, the solution loses these properties and contains only iodate and iodide : $3OI' \cdot IO_3' + 2I'$. Free hypo-iodous acid is formed on shaking a solution or a suspension of finely powdered iodine with precipitated mercuric oxide and filtering :



The acid is very weak and has been supposed to be amphoteric in character, functioning as a very weak base as well as a very weak acid:

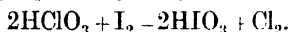


Iodic acid.—This is the most important oxy-acid of iodine. It is formed by the oxidation of iodine with ozone in presence of water, but is best prepared by boiling iodine with ten times its weight of fuming nitric acid (dens. 1.5) in a flask, evaporating to dryness, heating to 200° to expel nitric acid, and dissolving the iodine pentoxide formed in the smallest amount of warm water. On cooling the syrupy liquid, colourless rhombic crystals of iodic acid separate :

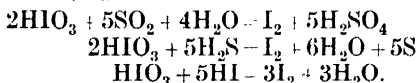


Iodic acid is formed by passing chlorine into a suspension of iodine in water : $\text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HIO}_3 + 10\text{HCl}$. Hydrochloric acid is removed as silver chloride by addition of silver oxide.

Iodic acid may be prepared by evaporating iodine with 25 per cent chloric acid :



Iodic acid is very soluble in water, but is not deliquescent. The solution first reddens and then bleaches litmus paper. Iodic acid is insoluble in alcohol. The solid deflagrates when heated with powdered charcoal, sulphur, phosphorus, or organic matter, and in solution the acid is an oxidising agent :



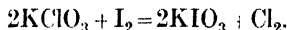
Iodic acid melts at 110° to form a solution and a solid hydrate $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ of I_2O_5 stable to 196° but then fusing to form I_2O_5 .

Iodates.—On adding iodine to hot concentrated alkali hydroxide solution an iodate and iodide are formed :



With potassium hydroxide, sparingly soluble potassium iodate KIO_3 crystallises on cooling.

Potassium iodate is also formed by heating iodine with a concentrated solution of potassium chlorate and a little nitric acid :



If barium chloride is added to a solution of potassium iodate, barium iodate is precipitated. This is decomposed by dilute sulphuric acid to form a solution of iodic acid : $\text{Ba}(\text{IO}_3)_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HIO}_3$.

Iodic acid, although monobasic, forms normal salts and two acid salts :

Normal potassium iodate KIO_3

Acid potassium iodate $\text{KIO}_3 \cdot \text{HIO}_3$ or $\text{KH}(\text{IO}_3)_2$

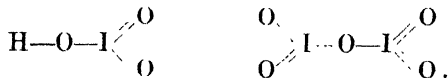
Diacid potassium iodate $\text{KIO}_3 \cdot 2\text{HIO}_3$ or $\text{KH}_2(\text{IO}_3)_3$.

The acid salts are isomorphous with acid salts of some dibasic organic acids (succinic, etc.). The normal iodates are sparingly soluble or insoluble in water. On heating, they decompose : (i) into iodide + oxygen, e.g. KIO_3 , (ii) into oxide + iodine + oxygen, e.g. $\text{Ca}(\text{IO}_3)_2$.

Barium iodate forms a periodate on heating (see below). Iodates form complex compounds with molybdic, tungstic, selenic, sulphuric and phosphoric acids.

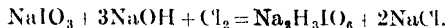
Iodates are detected by the blue colour, due to liberation of iodine, when sulphurous acid and starch-paste are added to a solution.

The formula of iodic acid and iodine pentoxide are written on the assumption that these compounds contain quinquevalent iodine :

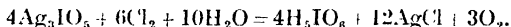


Periodic acid.—Periodic acid, discovered by Ammermüller and Magnus in 1833, is formed by the electrolytic oxidation of iodic acid, but is most conveniently prepared by the following method.

A sodium periodate $\text{Na}_2\text{H}_3\text{IO}_6$ (mixed with $\text{Na}_4\text{H}_2\text{IO}_6$) is precipitated on oxidising a boiling solution of 12.7 gm. of iodine in a 10 per cent solution of 60 gm. of sodium hydroxide, with a rapid stream of chlorine :



A suspension of this salt in water is heated with silver nitrate at 100° , giving a black precipitate of silver mesoperiodate Ag_3IO_5 , which is washed, suspended in water, and decomposed by chlorine, giving silver chloride and a solution of periodic acid which is evaporated in a vacuum desiccator over concentrated sulphuric acid, when colourless deliquescent crystals of paraperiodic acid H_5IO_6 (the common periodic acid) are formed :



The crystals of paraperiodic acid melt with decomposition on heating : $2\text{H}_5\text{IO}_6 = 2\text{HIO}_4 + 4\text{H}_2\text{O} + \text{O}_2$, but below 100° in a vacuum they lose water, forming dimesoperiodic acid $\text{H}_4\text{I}_2\text{O}_9$, and then metaperiodic acid HIO_4 . The latter slowly sublimes. (Bahl and Partington, 1934).

Barium periodate $\text{Ba}_5(\text{IO}_6)_2$ is very stable and is formed on heating barium iodate to redness : $5\text{Ba}(\text{IO}_3)_2 = \text{Ba}_5(\text{IO}_6)_2 + 4\text{I}_2 + 9\text{O}_2$. A solution reacts with dilute sulphuric acid with formation of a solution of periodic acid : $\text{Ba}_5(\text{IO}_6)_2 + 5\text{H}_2\text{SO}_4 = 2\text{H}_5\text{IO}_6 + 5\text{BaSO}_4$.

Solutions of periodic acid and periodates are powerful oxidising agents, converting manganous salts into permanganate. The periodates are usually sparingly soluble. A solution of KIO_4 gives with silver nitrate a brown precipitate of AgIO_4 , soluble in dilute nitric acid. Several groups of periodates known may be regarded as derived from acids formed by loss of water from a hypothetical ortho-acid $\text{I}(\text{OH})_7$. They all contain septavalent iodine :

PERIODIC ACIDS

ortho- $\text{I}(\text{OH})_7$, unknown

para- $\text{IO}(\text{OH})_5$ or H_5IO_6

meso- $\text{IO}_2(\text{OH})_3$ or H_3IO_5 , unknown

dimeso- $(\text{HO})_2\text{IO}_2\text{OIO}_2(\text{OH})_2$ or $\text{H}_4\text{I}_2\text{O}_9$

meta- $\text{IO}_1(\text{OH})$ or HIO_4

PERIODATES

unknown

$\text{Ba}_5(\text{IO}_6)_2$; $\text{Na}_2\text{H}_3\text{IO}_6$;

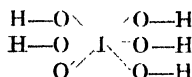
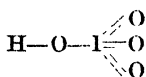
$\text{Na}_3\text{H}_2\text{IO}_6$; $\text{Ag}_2\text{H}_3\text{IO}_6$

Ag_4IO_6

$\text{Na}_4\text{I}_2\text{O}_9$; $\text{Ag}_4\text{I}_2\text{O}_9$

KIO_4 ; AgIO_4 .

Structural formulae are :



In the IO_6^{5-} ion the six oxygen atoms are arranged octahedrally with six identical bonds around the iodine atom.

FLUORINE

History.—The mineral *fluorite* or *fluorspar* occurs in Derbyshire, crystallised in cubes or octahedra or in compact masses like marble. It is called “Derbyshire Spar”, or “Blue John” when the crystals are coloured blue or purple. Colourless transparent crystals show a bluish tinge when light falls on them, and this property (shown by petroleum, solutions of quinine salts, and other substances) is called *fluorescence*. Fluorspar was described by Agricola (1530) as *fluor*, from the Latin *fluo*, I flow, since it melts at a red heat (1330°). Fluorspar is calcium fluoride, CaF_2 .

The composition of fluorspar was for long unknown. It appears that crude hydrofluoric acid was first prepared by an unknown English glass-worker about 1720. Scheele, in 1771, discovered that fluorspar is a salt of lime and a peculiar acid, which he obtained in an impure state by distilling fluorspar with concentrated sulphuric acid in a glass retort. The retort was powerfully corroded and a gas formed which deposited gelatinous silica on passing into water. J. C. F. Meyer (1781) and C. F. Wenzel (1783) used iron and lead vessels and obtained fairly pure hydrofluoric acid solution, the part played by the silica from glass being clearly recognised. In 1786 Scheele used a tin retort. Gay-Lussac and Thénard, who investigated the acid in 1809, regarded it as the oxide of an unknown radical. Ampère in 1810 suggested that it is a compound of hydrogen with an unknown element **fluorine**, analogous to chlorine. The element was first isolated by Moissan in 1886.

Occurrence.—Fluorine is widely distributed as fluorspar and other fluorides. Large quantities of *cryolite* Na_3AlF_6 are found in Greenland, and *fluor-apatite* $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$ is common. Small quantities of calcium fluoride in soil (probably derived from apatite) are absorbed by plants, the ashes of which contain about 0.1 per cent of fluorine. From plants calcium fluoride passes into the bones and teeth of animals, especially the hard parts; enamel of teeth may contain 0.3 per cent of fluorine, possibly as apatite.

The blue colour of some kinds of fluorspar is usually due to organic matter. On heating it disappears. Some blue varieties contain free fluorine. Colourless fluorspar becomes blue when exposed to radium emanation.

Preparation.—The isolation of fluorine was for long one of the master problems of inorganic chemistry. The attempts of Davy, Fremy, Nicklès, Louyet, and Gore towards its solution were uniformly unsuccessful. If platinum vessels were used a chocolate-coloured powder, PtF_4 , was obtained; carbon vessels were attacked with the formation

of a gaseous fluoride CF_4 . Attempts to electrolyse hydrofluoric acid met with no success: if the aqueous acid was used only oxygen and hydrogen were obtained, whilst the anhydrous acid is a non-conductor or Moissan in 1886 found that anhydrous hydrofluoric acid becomes an electrolyte when potassium hydrogen fluoride KHF_2 is dissolved in it. If this solution is electrolysed in a U-tube of an alloy of platinum and iridium with electrodes of the same material, the whole being strongly cooled, hydrogen is evolved from the cathode and fluorine from the anode. In 1899 Moissan found that the platinum apparatus could be replaced by copper, which apparently becomes coated with a protecting film of fluoride. The electrodes must still be of platinum-iridium.

On the left in Fig. 178 is the U-tube, of 300 ml. capacity, containing 60 gm. of acid potassium fluoride dissolved in 200 ml. of anhydrous hydro-

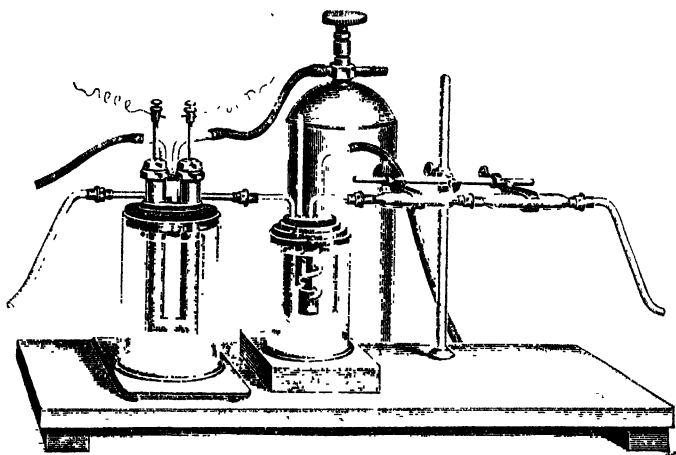
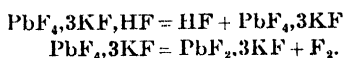


FIG. 178.—Moissan's apparatus for preparing fluorine.

fluoric acid. The electrodes are insulated by fluorspar stoppers covered outside with shellac. The tube is immersed in a bath of methyl chloride, b. pt. -23° , which is constantly renewed, and a potential of 50 volts is applied. The fluorine from the anode (about 5 litres per hour) is passed through a platinum or copper spiral cooled in methyl chloride, and a tube of the same metal packed with fused sodium fluoride, to remove hydrofluoric acid. By collecting and measuring the hydrogen from the cathode, and absorbing the fluorine in iron wire in a weighed platinum tube, Moissan found that for every gram of hydrogen evolved the iron increased in weight by 19 grams. The gas was therefore free fluorine.

Brauner (1894) obtained small quantities of fluorine by heating potassium fluorplumbate $PbF_4 \cdot 3KF \cdot HF$, made by the action of hydrofluoric acid on potassium plumbate. At 230° – 250° this loses hydrofluoric acid and at higher temperatures free fluorine:



Fluorine is more easily prepared by the electrolysis of fused acid potassium fluoride in a copper vessel with graphite electrodes. The electrolyte, pure and dry KHF_2 (m. pt. 217°), is fused in an electrically heated vessel, such as a wide copper V-tube AA (Fig. 179); the electrodes RR are pure Acheson graphite rods insulated in Bakelite cement stoppers BB . A current of 5 amp. at 12 volts is used. The fluorine (0.92 litre per hour) is purified by passage through two copper U-tubes FG , containing dry sodium fluoride (Dennis, Veeder and Rochow, 1931). Purity of the salt and of the electrodes is essential.

Fluorine can be made on the industrial scale. The common electrolytes are fused acid potassium fluorides with carbon anodes, and up to 2,000

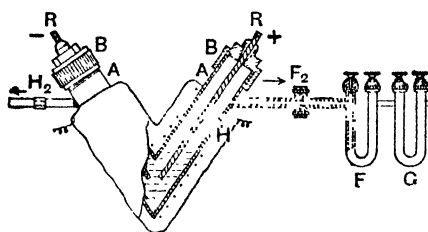


FIG. 179.—Preparation of fluorine.

amperes were used in the electrolysis currents. An anode current efficiency of about 95 per cent was attained. The gas can be piped in steel or copper, and compressed up to 400 lb./in.² in nickel and steel cylinders. Purification reached 98 per cent minimum.

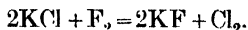
Fluorination of hydrocarbons formed numerous products up to $\text{C}_{18}\text{F}_{33}$, and much use was made of cobalt trifluoride CoF_3 , and silver difluoride AgF_2 . The fluorine-hydrogen blowpipe is used for welding metals.

Properties.—Fluorine is a pale greenish-yellow gas, with very little action on glass below 100° , so that it may be kept in glass vessels. It has a powerful odour resembling hypochlorous acid, but is not so poisonous as hydrofluoric acid vapour. By weighing the gas in a glass flask, Moissan found the density 18.91 ($\text{H} = 1$), from which the formula F_2 follows. Fluorine was liquefied in 1897 by Moissan and Dewar, who cooled the gas in liquid air boiling in a vacuum. The liquid is clear yellow, b. pt. -187° , density 1.108 at the b. pt. By cooling in liquid hydrogen, Dewar (1903) obtained pale-yellow solid fluorine, m. pt. -233° , becoming colourless at -252° .

Fluorine fumes in moist air, forming hydrofluoric acid and ozone. Fluorine is the most active element known. It does not react directly with oxygen or nitrogen, and combines with chlorine only on heating, forming gaseous ClF and ClF_3 . It readily combines with bromine and iodine, forming colourless liquids BrF_3 and IF_5 .

A jet of fluorine ignites at once in a jar of hydrogen, burning with a red-bordered flame and producing HF , which attacks the glass jar. Fluorine unites with moist hydrogen explosively even at -252° , but the very pure and dry gases do not react at room temperature. Boron, carbon (as charcoal), silicon, phosphorus, arsenic, antimony, bromine, iodine, sulphur, selenium, tellurium, and potassium all ignite spontaneously in the gas and burn with the formation of fluorides. Silver, magnesium, zinc, aluminium, tin, manganese, iron, and nickel take fire when gently warmed. Lead is only slowly attacked at the ordinary temperature, and copper becomes coated with a protective layer of

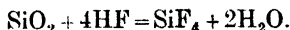
fluoride. Gold and platinum are not attacked at the ordinary temperature but are corroded and form fluorides on heating. Alcohol, ether, and turpentine take fire spontaneously in the gas. Potassium chloride is decomposed with evolution of chlorine :



Fluorine can replace oxygen in many acids without producing much change in chemical properties, *e.g.* it forms fluoriodates MF_2IO_2 , and $\text{IF}_3(\text{OH})_2$, and replaces oxygen in niobates and tantalates.

Hydrofluoric acid.—Hydrogen and fluorine combine when moist to form hydrogen fluoride or hydrofluoric acid HF, which is more conveniently made by the action of sulphuric acid on fluorides or by heating acid potassium fluoride.

Powdered fluorspar is distilled with 90 per cent sulphuric acid in a lead retort connected with a lead receiver containing water, in which the vapour of hydrofluoric acid dissolves : $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. The colourless solution is kept in wax or gutta-percha bottles, and is used for etching or engraving on glass, which consists of alkali and alkaline earth silicates ; hydrofluoric acid removes the silica in the form of silicon fluoride :



Etchings with the liquid acid are clear ; those made with the gas or a mixture of aqueous acid and ammonium fluoride are opaque.

A watch-glass is covered with beeswax by melting and draining off the liquid. When the wax has hardened, a device is scratched through with a needle and the glass placed over a lead dish containing a mixture of powdered fluorspar and concentrated sulphuric acid, gently warmed. The parts of the glass exposed are seen to be etched if the wax is removed after a few minutes by warming the glass.

The commercial acid, dens. 1.130, contains about 40 per cent of HF. It is used for etching glass, for removing silica from canes and sand from castings, and as an antiseptic. The "wild yeasts" which produce fusel oil in fermentation are killed by small quantities of sodium fluoride, whilst normal yeast-cells may be accustomed to it. Lactic and butyric fermentations are also inhibited. Zinc and sodium fluorides are used in preserving wood.

Almost pure anhydrous hydrofluoric acid is made in America from fluorspar and transported in steel containers.

If aqueous hydrofluoric acid is neutralised with potassium hydroxide and the liquid evaporated in a platinum dish, cubic crystals of potassium fluoride KF are obtained. If a further equal volume of hydrofluoric acid is added to the neutralised liquid and the liquid evaporated in a platinum dish, crystals of potassium hydrogen fluoride KHF_2 called *Freymy's salt* (it was actually discovered by Berzelius) are obtained. This may be dried by heating and is relatively stable. If it is heated in a platinum or copper retort, connected with a condenser of the same metal cooled by a freezing mixture, anhydrous hydrofluoric acid distils

(Fig. 180) : $\text{KHF}_2 = \text{KF} + \text{HF}$. The anhydrous acid was first prepared in this way by Fremy in 1856.

Anhydrous hydrofluoric acid is a colourless strongly-fuming liquid, dens. 0.988, boiling at 19.4° ; it should be kept in a platinum bottle in a freezing mixture. It does not solidify until cooled to -102° ; the transparent colourless solid melts at -83° . When quite free from water the liquid acid is said not to attack glass or metals at the ordinary temperature, except potassium, which explodes in contact with it. According to Moissan, the dry *gas* attacks glass. In presence of a trace of water the acid attacks glass violently, and dissolves most metals with evolution of hydrogen : $\text{Fe} + 2\text{HF} = \text{FeF}_2 + \text{H}_2$. The noble metals are not attacked, but gutta-percha (which resists the aqueous acid) and

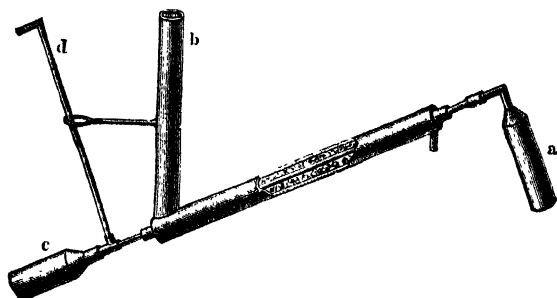


Fig. 180. Platinum retort and condenser for preparing anhydrous hydrofluoric acid.

most organic materials are rapidly corroded. Ceresin wax, or polythene (polymerised ethylene), bottles resist the concentrated acid. The acid and its vapour are dangerous corrosive poisons. They attack the skin violently and form sores which heal only with great difficulty, hence rubber gloves should be worn in manipulating the acid.

Hydrofluoric acid forms a solution of maximum boiling point, 120° , containing 36 per cent of HF.

The *composition of hydrofluoric acid* was determined by Gore (1869), who heated silver fluoride at 100° in hydrogen in a platinum vessel and obtained twice the volume of hydrofluoric acid gas. The formula at 100° is therefore HF : $2\text{AgF} + \text{H}_2 = 2\text{HF} + 2\text{Ag}$. Mallet (1881) by weighing the vapour at 30.5° in a glass flask coated inside with paraffin wax obtained the density 19.66 ($\text{H} = 1$) corresponding with the formula H_2F_2 . Thorpe and Hambly (1889) by determining the vapour densities in a platinum flask at various temperatures and pressures, showed that the gas is associated, the density varying with temperature and pressure. At 88° and 741 mm. the molecular weight corresponds with HF; at lower temperatures it approximates to H_2F_2 . No indication of the separate existence of H_2F_2 was found, the density falling continuously with rise of temperature or diminution of pressure to the limiting value corresponding with HF. Simons and Hildebrand (1924) concluded from measurements of vapour pressure and density that the gaseous acid at temperatures of 15° to 19° C. is a mixture of H_2F_2 .

and HF molecules in equilibrium, but Thorpe and Hambly's results have been confirmed by Fredenhagen (1934).

In concentrated solutions the acid appears to be H_2F_2 , but in dilute solutions freezing-point measurements give the formula HF, and the existence of H_2F_2 molecules is doubtful, although the liquid acid is associated.

The fluorides differ in many ways from other halogen compounds. Silver fluoride is very soluble, calcium fluoride is nearly insoluble, in water. The iron compound corresponding with cryolite, viz. Na_3FeF_6 , is insoluble. If a standard solution of a ferric salt is added to a solution of sodium fluoride, this compound is precipitated, and if a little ammonium thiocyanate is added the excess of ferric salt gives a red colour. Fluorides may be titrated in this way.

Many fluorides readily form complex compounds with hydrofluoric acid, e.g. HBf_4 , H_2SiF_6 , H_2NbOF_5 , etc., which form salts, KBF_4 , K_2SiF_6 , K_2NbOF_5 .

Ammonium fluoride NH_4F , obtained by neutralising the acid with ammonium carbonate, decomposes on fusion and forms the acid fluoride: $2NH_4F = NH_3 + NH_4HF_2$.

Fluorine oxides.—Lebeau and Damiens (1927) found that gaseous fluorine monoxide F_2O is produced by passing fluorine at the rate of 1 litre per hour through 2 per cent sodium hydroxide solution: $2F_2 + 2NaOH = 2NaF + F_2O + H_2O$. It may be collected over water and liquefied in liquid air, b. pt. -146.5° , m. pt. 223.8° . It is a stable gas, which is a powerful oxidising agent, liberating iodine from potassium iodide solution, which completely absorbs it: $F_2O + 4KI + H_2O = 2KF + 2KOH + 2I_2$. Difluorine dioxide F_2O_2 is an orange-red solid, m. pt. -163.5° , obtained by the action of an electric discharge on a mixture of fluorine and oxygen at low temperature and pressure (Ruff, Menzel and Clusius, 1930). Above -100° the pale-brown gas decomposes into fluorine and oxygen.

Compounds of fluorine with other halogens.—Chlorine monofluoride (ClF is a colourless gas (m. pt. -161° , b. pt. -103°) formed from hydrogen fluoride and chlorine at liquid air temperature, or by heating fluorine and chlorine in a copper vessel at 250° . It reacts with some metals even more vigorously than fluorine itself. With excess of fluorine chlorine trifluoride (ClF₃ (m. pt. -83° , b. pt. $+11.3^\circ$) is formed; this attacks glass very vigorously.

Bromine trifluoride BrF₃ is formed from fluorine and bromine or hydrogen bromide as a colourless fuming liquid, m. pt. -2° , b. pt. 127° ; bromine pentafluoride BrF₅ is formed from the elements at 0° , m. pt. -61.3° , b. pt. 40.5° , the vapour being stable at 460° ; bromine monofluoride BrF is a reddish-brown unstable gas, m. pt. -33° , b. pt. c. 20° , formed from the trifluoride and bromine.

A liquid iodine pentafluoride IF₅ (m. pt. 8° , b. pt. 97°) is formed by direct combination of the elements, by the action of fluorine on heated iodine pentoxide, or by heating iodine with silver fluoride (Gore, 1871). When heated with fluorine at $270^\circ - 300^\circ$ it forms gaseous iodine heptafluoride IF₇, b. pt. 4.5° , with the normal vapour density.

The halogens.—The elements fluorine, chlorine, bromine, and iodine are so related in chemical properties as to form a group or family, called the **halogen group** (Greek *hals* = salt). The properties of the free elements and of their hydrogen compounds show a marked gradation in the order given above. This is seen in the first place in the *physical properties of the elements* :

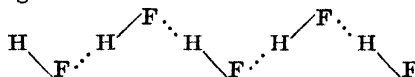
Element.	Atomic weight	Physical state.	Colour.	Melting point abs.	Boiling point abs.	Density of liquid.	Solubility in water gm./lit. at 0°.
F	19	gas F ₂	pale greenish-yellow	40°	86°	1.108	decomposes
Cl	35.5	gas Cl ₂	greenish-yellow (liquid)	172.2°	238.6°	1.55	14.6
Br	80	liquid Br ₂	dark red (vapour red)	265.9°	331.9°	3.19	41.5
I	127	solid I ₂	black (vapour violet)	386.6°	457.5°	4.9 solid	0.162

The *physical properties of the hydrogen compounds (all acids)* are :

Compound.	Melting point abs.	Boiling point abs.	Density of liquid.	Heat of formation in k cal.	Atomic distance A.U.	Energy of formation from atoms k. cal.
HF	180.8°	292.5°	0.988/15°	38.5	0.86	140
HCl	157.8°	188°	0.929/0°	22	1.28	102
HBr	185.0°	206°	2.16 (b. pt.)	12.1*	1.42	86
HI	222.2°	237.6°	2.80 (b. pt.)	-6.1†	1.6	66

The physical properties of hydrofluoric acid are abnormal ; it is *associated* even in the gaseous state below 80°, whereas the other substances are normal. Association leads to increase of boiling point. The energies of formation from the free atoms diminish and the distances between the centres of the atoms increase, with increasing atomic weight of the halogen.

It was formerly supposed that the associated molecules of hydrogen fluoride were (HF)₆, with the six HF units arranged in the form of a hexagonal ring. Electron diffraction by the gaseous acid (p. 439) shows that polymers ranging from (HF)₂ to (probably) (HF)₆ are present, and that they are of zig-zag form :



with the F—F distance 2.55 A., and the H—F—H bond angle 140°. Solid hydrofluoric acid also contains long zig-zag chains of molecules.

The interaction between one HF unit and the next, represented in the figure by a dotted line, is different from that of a normal covalent bond (p. 412), and is an example of what is called *hydrogen bonding*, the interaction leading to what are called *hydrogen bonds*, *hydrogen bridges*, or *proton bonds*. Such bonds are supposed to be present in the boron hydrides (p. 656).

The stability of the hydrogen compounds as measured by their dissociation on heating is in the order HF > HCl > HBr > HI, *i.e.* in the

* From $\frac{1}{2}$ (Br₂) gas.

† From $\frac{1}{2}$ [I₂] solid.

order of the heats of formation. Thus, hydrogen iodide is appreciably dissociated at 360° but hydrogen chloride only slightly at 1000° . The halogens displace one another from their binary salts in the order of the heats of formation, viz. : F -Cl -Br -I. In the oxygen compounds iodine can displace chlorine.

A summary of the general properties of the other compounds would merely be a repetition of information already given. Attention may be drawn to the decreasing stability of the acids HOX and their salts from chlorine, through bromine, to iodine, and the increasing stability of iodic acid as compared with chloric acid, bromic acid being anomalous. The unusual formula H_5IO_6 of the common periodic acid, and the non-existence of oxyacids of fluorine and of perbromic acid, should be noted.

CHAPTER XXI

ATOMIC HEATS AND ISOMORPHISM

The determination of atomic weights.—The methods used in deciding which multiple of the *equivalent* of an element is the *atomic weight* have already been referred to briefly (p. 110). The application of these methods gives a valuable check on the atomic weight. If the atomic weight has been fixed approximately from the specific heat, the vapour density of *one* volatile compound may be valuable confirmation, although it could not alone give a certain result, since it could not be assumed that the compound contains only one atom of the element.

ATOMIC HEATS.

Dulong and Petit's Law.—P. L. Dulong and A. T. Petit in 1819 discovered a simple relation between the atomic weight A and specific heat c of a *solid* element, viz., that the product of the atomic weight and specific heat, which they called the *atomic heat*, is constant, $Ac = \text{const.} = 6.3 \text{ g. cal.}$ Dulong and Petit's law asserts that *the atomic heats of solid elements are constant and approximately equal to 6.3 g. cal.* In some cases, especially metals, the constant is about 6.4. The table on p. 345 gives results determined near atmospheric temperature.

To obtain agreement with the law, Dulong and Petit had to alter some atomic weights current at the time: except in one or two cases these modifications have been confirmed.

Quantities of solid elements in the ratio of their atomic weights are raised through equal temperatures by identical quantities of heat. The heat capacity of a solid element is a property of its atoms, and Dulong and Petit expressed their result in the statement: *the atoms of all solid elements have the same capacity for heat.*

By assuming that the *mean* energy of a monatomic solid due to atomic vibration is half kinetic and half potential (as in small vibrations), and that the *kinetic* energies of the atom of the solid and that of a monatomic gas are equal at the same temperature (Maxwell's law of equipartition of energy), Boltzmann (1871) showed that the atomic heat of the solid should be twice that of the monatomic gas, viz. $2 \times 3 = 6 \text{ g. cal.}$ (p. 127).

The present exceptions to Dulong and Petit's law (which give atomic heats smaller than 6.3) are elements of *low atomic weight and high melting point*. Thus, sodium (at. wt. 23: m. pt. 97.6°) conforms to the law, beryllium (m. pt. 1280°), boron (m. pt. over 2000°), carbon (m. pt. over 3500°) and silicon (m. pt. 1420°), with atomic weights lower than 30, and high melting points, all have atomic heats appreciably smaller than 6.3.

TABLE OF ATOMIC HEATS

Element.	Atomic weight.	Specific heat. (20° to 100°).	Atomic heat = Atomic weight × Specific heat.
Arsenic - -	74.96	0.0827	6.22
Bismuth - -	208.0	0.0303	6.30
Bromine (solid) - -	79.92	0.0705	5.63
Calcium - -	40.07	0.149	5.97
Cobalt - -	58.97	0.1030	6.03
Copper - -	63.57	0.0928	5.90
Gold - -	197.2	0.0316	6.23
Iodine - -	126.92	0.0524	6.64
Iron - -	55.84	0.1096	6.12
Lead - -	207.2	0.0309	6.41
Lithium - -	6.94	0.94	6.52
Magnesium - -	24.32	0.2492	6.06
Mercury (solid) - -	200.6	0.0335	6.72
Nickel - -	58.68	0.1084	6.36
Phosphorus (white) - -	31.04	0.1981	6.20
Platinum - -	195.2	0.0320	6.25
Silver - -	107.88	0.0560	6.04
Sulphur - -	32.06	0.1751	5.61
Tin - -	118.7	0.0556	6.62
Uranium - -	238.2	0.0280	6.67
Zinc - -	65.37	0.0944	6.17

Atomic weights from specific heats.—Dulong and Petit's law gives an *approximate* value of the atomic weight of a solid element :

$$\text{Atomic weight} = 6.3 \div \text{Specific heat.}$$

A volatile chloride of uranium has the percentage composition : uranium, 62.66, chlorine, 37.34. The equivalent of uranium, the weight combining with 35.5 parts of chlorine, is $62.66 \div 35.5 = 1.765$. The vapour density of the chloride was found by Zimmermann to be 191 (H = 1), hence the *approximate* molecular weight is $191 \times 2 = 382$. This contains $37.34 \times 382/100 = 142.5$ parts, nearly equal to $4 \times 35.5 = 142$ parts or four atoms of chlorine. The formula of the chloride is U_xCl_4 , where $x = 1, 2, 3, 4 \dots$ etc.

The weight of uranium in a molecular weight of the chloride is *approximately* $382 - 142.5 = 239.5$, nearly equal to $4 \times 59.55 = 238.2$, i.e. four times the *accurately* determined equivalent. Thus $U_x = 238.2$. It has still to be decided whether this is the atomic weight of uranium, or a multiple of it. The following formulae of the chloride are possible :

Formula.	At. wt. of Uranium.
UCl_4	238.2
U_2Cl_4	119.1
U_3Cl_4	79.4
U_4Cl_4	59.55

The specific heat of solid metallic uranium is 0.02765 ; hence, by Dulong and Petit's law, the atomic weight of uranium is approximately $6.4 \div 0.02765 = 232$. This shows that the *exact* value is 238.2, and hence the **formula** of the chloride is UCl_4 .

It must be noted that the atomic weight from Dulong and Petit's law is only *approximate*, and is used to decide on a multiple of the *exact* equivalent.

Atomic heats at high temperatures.—Weber in 1875 found that the specific heats of boron, carbon, and silicon increase fairly rapidly with temperature, and the same was found for beryllium by Humpidge in 1885.

Diamond. °C. At. ht.	Graphite. °C. At. ht.	Boron. °C. At. ht.	Silicon °C. At. ht.	Beryllium. °C. At. ht.
- 50 0.76	- 50 1.37	- 40 2.11	- 40 3.81	0 3.42
10.7 1.35	10.8 1.92	26.6 2.62	21.6 4.75	100 4.28
58.3 1.84	61.3 2.39	76.7 3.01	86 5.32	200 4.93
140 2.66	201.6 3.56	177.2 3.63	184.3 5.63	300 5.38
247 3.63	249.3 3.90	233.2 4.33	232.4 5.68	400 5.61
615 5.33	640 5.40	—	—	500 5.65
808 5.44	832 5.42	—	—	—
980 5.47	980 5.63	—	—	—

At high temperatures the atomic heats approach the normal value 6.3 (Fig. 181). The atomic heats of some elements, which are normal at the ordinary temperature, also increase with temperature. The

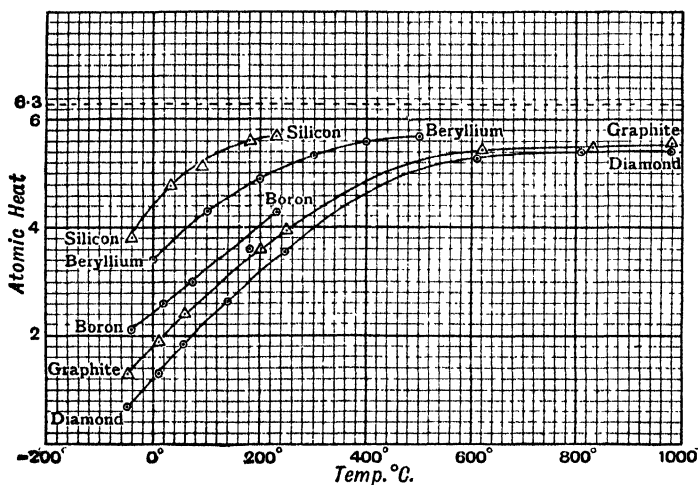


FIG. 181.—Atomic heat curves.

atomic heat of platinum in the interval 20° – 1300° is 7.01. Those of lithium at -50° , 0° , 100° and 190° are 4.83, 5.22, 7.22 and 9.54 respectively.

Atomic heats at low temperatures.—The atomic heats of *all* solid elements decrease to small values at low temperatures, some more rapidly than others, and at the absolute zero (-273°) the atomic heats are probably all zero. In the case of diamond, the atomic heat is actually zero at finite temperatures below -230° .

Element.	Atomic heat +20° to 100°.	Atomic heat -188° to +20°.	Atomic heat -253° to -195°.
Carbon	- - 2.4	1.15	0.03
Aluminium	- - 5.9	4.73	1.12
Silicon	- - 5.2	3.34	0.77
Iron	- - 6.4	4.80	0.98
Copper	- - 6.0	5.01	1.56
Zinc	- - 6.1	5.53	2.52
Silver	- - 6.1	5.51	2.62
Lead	- - 6.4	6.21	4.96

The atomic heats of diamond are :

Temperature °C.	- 896	85	- 41	- 64	- 181	- 231	- 243
Atomic heat	- 5.45	2.12	0.86	0.66	0.03	0.00	0.00

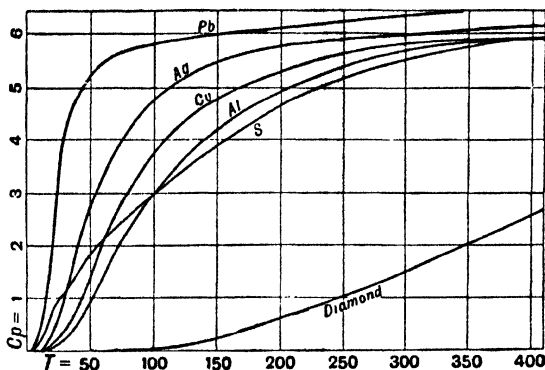


FIG. 182.—Atomic heats at low temperatures.

The following results were obtained by Kamerlingh Onnes and Keesom (1915), at the temperatures of liquid hydrogen :

Lead.		Copper.	
Temp. abs.	Atomic heat.	Temp. abs.	Atomic heat.
14.19°	1.56	15.24°	0.0500
22.31°	2.98	21.505°	0.1414
46.25°	5.04		

The dependence of atomic heat on temperature is shown for a few elements in the curves of Fig. 182 from the experiments of Nernst.

The quantum theory of the specific heats of solids.—The rapid fall in the specific heats of solids at low temperatures, and the convergence to zero near the absolute zero, is predicted by the quantum theory of Planck (1900). According to this, the atoms in a solid do not take up heat energy continuously but in finite quanta. The value of the quantum ϵ varies from element to element and is equal to $h\nu$, where h is a universal constant equal to 6.6×10^{-27} erg sec., known as Planck's constant, and ν is the atomic frequency, characteristic of each element, and the frequency of atomic vibration in the solid.

The "deviations" from Dulong and Petit's law at low temperatures are explained by the theory; this law is a limiting case of a more general law, and is approximately true only at higher temperatures. According to Einstein (1907) the atomic heat of a monatomic solid element is given by

$$\text{Atomic heat} = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$

where $x = h\nu/kT$, h being Planck's constant and k Boltzmann's constant, or the gas constant per molecule, $k = R/N$, where R is the molar gas constant in absolute units and N is Avogadro's number.

The atomic heat in this formula is that at constant volume, $C_v = Ac_v$, whilst those in the table on p. 345 are at constant pressure, $C_p = Ac_p$, and are rather larger than the theoretical value.

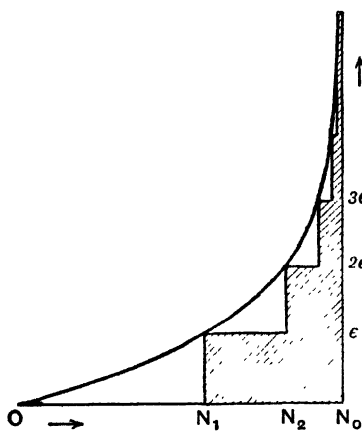


FIG. 183. Energy distribution among aluminium atoms at 300° abs.

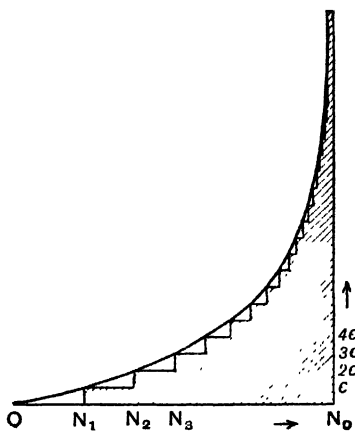


FIG. 184. Energy distribution among lead atoms at 300° abs.

It follows that when ν (and therefore x) is very small and T is not too small, $e^x \approx 1 + x$, hence $x^2 e^x / (e^x - 1)^2 \approx 1$, or the atomic heat is $3R$, the value required by Dulong and Petit's law, since in heat units (p. 121) R is 1.988, hence $3R = 5.96$ g. cal./1°. The atomic heats at constant volume, Ac_v , are often in good agreement with this value (G. N. Lewis, 1907).

The increase of C_p above $3R = 5.96$ at high temperatures is due to the heat capacity of the electrons in a metal, and theory shows that in such a case $C_p = 3R + CT$ ($C > 0$). Thus the curves when extrapolated to $T = 0$ should give the value 5.96. This is confirmed for platinum and copper.

When the quantum is large there is less energy absorbed than if absorption were continuous, and the atomic heat is abnormally low. These results are shown graphically in Figs. 183-4, in which the ordinates give the number of quanta absorbed and the abscissae (in which N_1 atoms out of a total of N_0 have no energy, $N_2 - N_1$ have one quantum (ϵ), $N_3 - N_2$ have two quanta (2ϵ), etc.) are such that the area under the curve is proportional to the energy content. The continuous curve represents the result for continuous absorption (total area $= 3RT$: Dulong and Petit's law). It is seen that the

shaded area (quantum absorption) is only a small fraction of that under the curve when the quantum is large (aluminium) but very nearly this area when the quantum is small (lead). This is in agreement with the figures in the table on p. 347.

According to Debye (1912) the atomic heat of a solid at very low temperatures is proportional to the cube of the absolute temperature, $At. ht. = aT^3$. This was confirmed by Nernst and others.

Molecular heat of a compound.—An extension of Dulong and Petit's law was made by F. Neumann in 1831, who found that *the specific heats of solid compounds of similar composition are inversely proportional to their molecular weights*. Thus :

Substance.	Molecular weight.	Specific heat.	Molecular heat.
Calcium carbonate, $CaCO_3$ -	100	0.2044	20.44
Magnesium carbonate, $MgCO_3$ -	84	0.2270	19.1
Ferrous carbonate, $FeCO_3$ -	116	0.1819	21.1
Zinc carbonate, $ZnCO_3$ -	125	0.1712	21.4
Barium carbonate, $BaCO_3$ -	196	0.108	21.1
Lead carbonate, $PbCO_3$ -	266	0.081	21.6

The molecular heat of a solid compound is the specific heat multiplied by the molecular weight, and Neumann's law shows that *the molecular heats of similar compounds are equal*. The molecular heats of the carbonates of the general formula RCO_3 are approximately 20; the sulphates RSO_4 of the same metals have a molecular heat of about 25.

The relation between Neumann's and Dulong and Petit's laws was pointed out by Joule in 1844. **Joule's law** (often called Woestyn's law) states that *the molecular heat of a solid compound is the sum of the atomic heats of its constituents*.

This was confirmed by Kopp (1865). It indicates that the heat content of a solid resides in its *atoms*. With gases the case is different, since the kinetic energy of the *molecule* is predominant.

The molecular heat of lead iodide may be calculated from the sum of the atomic heat of lead and twice the atomic heat of iodine: $PbI_2 : 6.41 + 2 \times 6.64 = 19.69$. The observed value is: $(Pb + 2I) \times sp. ht. of lead iodide = (207 + 2 \times 127) \times 0.0427 = 19.68$.

Joule's law gives the atomic heats of elements in the solid state in cases where these cannot be directly determined.

Specific heat of silver chloride = 0.091; \therefore molecular heat of $AgCl = 0.091 \times (108 + 35.5) = 13.01$. This is the sum of the atomic heats of silver and of solid chlorine; hence atomic heat of solid chlorine

$$\begin{aligned} & \text{molecular heat of silver chloride} - \text{atomic heat of silver} \\ & = 13.01 - 6.04 = 6.97. \end{aligned}$$

From the molecular heats of compounds, Kopp deduced the following atomic heats :

Boron - - -	2.7	Phosphorus - - -	5.4
Carbon - - -	1.8	Sulphur - - -	5.4
Silicon - - -	3.8	Oxygen - - -	4.0

These agree with the determined values at 0°–100° (except for oxygen), although they are all abnormal. The abnormal atomic heats are therefore preserved in combination.

CRYSTALLOGAPHY

Crystals.—A distinction is drawn between *crystalline* and *amorphous* substances. The most obvious difference is that of *external form*: amorphous solids are found in irregularly-shaped pieces; crystals usually have definite shapes. Another difference is in the *fracture*: crystals break into pieces with plane faces meeting in sharp edges, whilst amorphous solids such as glass or pitch break into very irregular pieces, showing curved faces with concentric rings such as are seen inside an oyster-shell. These two kinds of fracture are known as *crystalline fracture* and *conchoidal fracture*, respectively.

With the exception of crystals of the regular system (see below) all fragments of crystals act on polarised light, and if the powder is examined under a microscope so that the light enters a pair of crossed Nicol prisms, and is therefore totally extinguished, light passes through the interposed crystal grains, which are seen coloured on a dark ground.

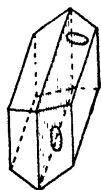


Fig. 185.—Gypsum crystal showing plane of symmetry.

Again, if a crystal of gypsum is touched with a red-hot needle on one face, a white patch of anhydrous calcium sulphate develops (Fig. 185): $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$. This patch is elliptical, showing that heat is conducted more readily in one direction than in the perpendicular direction.

We thus recognise definite **internal structure** in the crystal, which determines the outer form. Even if the outer form is destroyed by powdering, the internal structure remains. If the above experiments are tried with a piece of glass, no light passes the crossed Nicols, and if the glass is coated with paraffin wax the latter is melted in a circular patch when touched with a hot needle. The internal structure is more important than the external form.

The internal structure of a crystal is due to a definite, ordered arrangement of the atoms, ions, or molecules, and this arrangement can be detected by the effect of the crystal, even in powder form, on X-rays. The molecular structure is in general *symmetrical*—a definite pattern is repeated over and over again in definite directions in space, in the same way as the pattern of wall-paper in two dimensions. The internal symmetry corresponds with an external symmetry of the crystal form.

Symmetry of crystals.—The symmetry of a crystal form is determined by regularities in the positions of the similar faces, edges, etc. A crystal having all its faces alike is a **simple form**: both the cube and octahedron in Fig. 186 are simple forms, because all faces of the first are identical squares, and all those of the second are identical equilateral triangles. A crystal having sets of faces corresponding with two or more simple forms is called a **combination form**: the crystal of galena

shown in Fig. 186 is a combination of the cube and the octahedron and contains sets of faces derived from each.

The regularities in the positions of faces, edges, etc., are defined in terms of **planes of symmetry**, **axes of symmetry**, and a **centre of symmetry**.

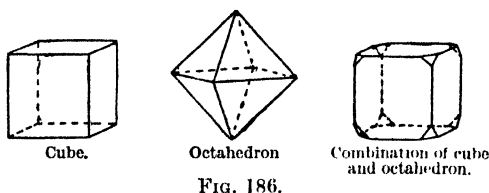


FIG. 186.



Fig. 187.—Epsom salt Crystal.

A plane of symmetry divides a perfect crystal into two similar and similarly-placed halves, each the mirror-image of the other. Thus, a crystal of gypsum is divided by the plane shown in Fig. 185 into two such halves, and this is the only plane of symmetry possessed by the gypsum crystal. An n -fold (or n -gonal) axis of symmetry is an axis such that a crystal rotated around it occupies the same position in space n times in a complete turn. The axis shown in Fig. 188 is an axis of fourfold symmetry, since the cube takes up the same position four times on rotation through 360° about this axis. Axes of two-, three-, four-, and six-fold symmetry occur, when the crystal comes to occupy the same position in space 2, 3, 4, or 6 times in a complete revolution, i.e. on rotation through 180° , 120° , 90° , or 60° .

The Epsom salt crystal in Fig. 187 appears to have an axis of *two*-fold symmetry. But if the right-hand upper sloping face is rotated through 90° and then supposed reflected in a horizontal plane, we obtain the lower left-hand sloping face as a virtual image. This crystal is said to have an *alternating axis of fourfold symmetry*.

A **polar axis** is one such that the groupings of faces about its two ends are different. The quartz crystals in Fig. 345 have polar axes.

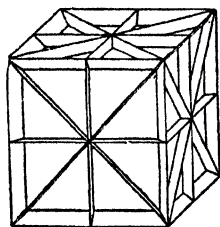


FIG. 189.—Planes of symmetry of cube.

A crystal has a **centre of symmetry** when like faces are arranged in pairs in corresponding positions on opposite sides of a central point.

A cube has 9 planes of symmetry (Fig. 189), 13 axes of symmetry (3 of fourfold, 4 of threefold, and 6 of twofold symmetry), and a centre of symmetry. It has 23 **elements of symmetry**, the highest number possible in a crystal. Some crystals have no plane of symmetry, others no axes of symmetry, others no centre of symmetry, and some have no element of symmetry at all.

The crystallographic symmetry depends on the internal structure and need not correspond with the geometrical symmetry except in the perfect crystal, since the crystal may have certain faces developed to a greater extent than others. The angles between the faces, however, are the same both

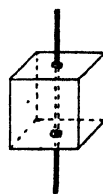


Fig. 188. Axis of symmetry of cube.

in the ideal crystal and in the distorted crystals, and these angles are important in determining the crystal form. The angles between the faces of the perfect and distorted octahedra in Fig. 190 are identical.

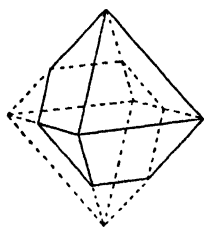


FIG. 190.—Ideal and distorted octahedra, showing constancy of angles between the faces.

This law of constant interfacial angles was enunciated by Nicolas Steno in 1669. It is approximate, since slight differences in interfacial angle may occur in different crystals of the same substance.

Crystal systems.—A simple classification of crystal forms is into crystal systems, related to the crystal axes. The position of any crystal face is defined by intercepts made on three axes intersecting in a point inside the crystal. If a suitable number of axes of symmetry exists, three may be chosen as crystal (crystallographic) axes, but the latter need not be axes of symmetry.

Six types of crystallographic axes are usually chosen :

(1) *Three equal axes at right angles* : this corresponds with the cubic or regular system.

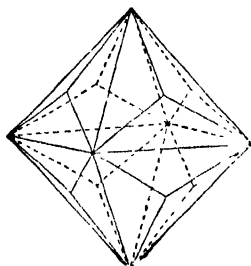


FIG. 191.—Triakis octahedron (three-faced octahedron).

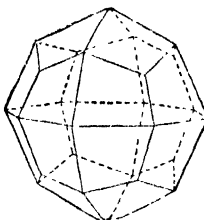


FIG. 192.—Icositetrahedron.

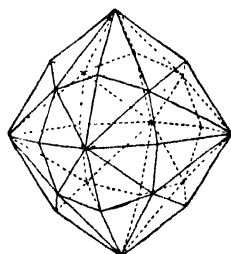


FIG. 193.—Hexakis octahedron (six-faced octahedron).

Fig. 196 I. shows the regular octahedron, the typical pyramid form of the regular system, and the cube, the typical prism form.

The other simple forms of the system are the triakis octahedron (Fig. 191), the icositetrahedron (Fig. 192), the hexakis octahedron (Fig. 193), the rhombododecahedron (Fig. 194), and the tetrakis hexahedron (Fig. 195).

Combinations of these forms also occur.

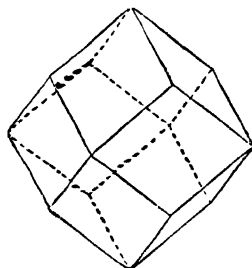


FIG. 194.—Rhombododecahedron.

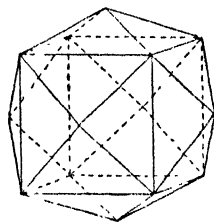


FIG. 195.—Tetrakis hexahedron (four-faced cube).

(2) *Two equal axes meeting at right angles and a third longer or shorter axis*

meeting these at right angles. This constitutes the tetragonal system. Typical pyramid and prism forms are shown in Fig. 196 II. There are two orders of pyramid and prism forms, according as the horizontal axes terminate at the angles or the middle point of the faces.

If the length of the vertical axis is denoted by c and the lengths of the horizontal axes by a and b , with appropriate signs, the cubic system may be denoted by $(a a a)$ and the tetragonal system by $(a a c)$.

(3) In the hexagonal system there are four axes, three equal and intersecting in the same plane at angles of 60° , and a fourth axis, greater or less than these, at right angles $(a a a c)$. There are two types of pyramid and prism forms, according as the lateral axes meet angles or the mid-points of faces. Typical pyramid and prism forms are shown in Fig. 196 III.

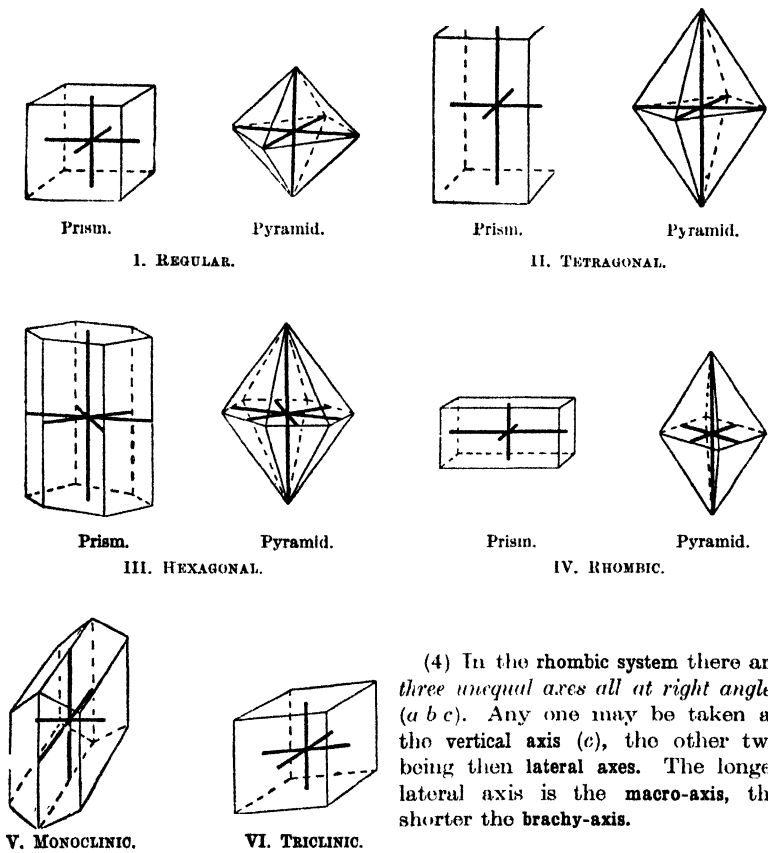


FIG. 196.—Crystal systems.

(4) In the rhombic system there are three unequal axes all at right angles $(a b c)$. Any one may be taken as the vertical axis (c), the other two being then lateral axes. The longer lateral axis is the macro-axis, the shorter the brachy-axis.

Pyramid and prism forms exist (Fig. 196 IV.), and new types of faces known as domes and pinakoids appear. Prism faces developed parallel to

one of the lateral axes, and intersecting the other two axes, are **dome faces**. Those parallel to the longer or macro-axis are **macrodomes**; if parallel to the shorter or brachy-axis they are **brachydomes** (Fig. 197).

Prism faces intersecting one lateral axis and parallel to the other two axes are **pinakoid faces**; **macropinakoids** intersect the macro-axis and **brachy-**

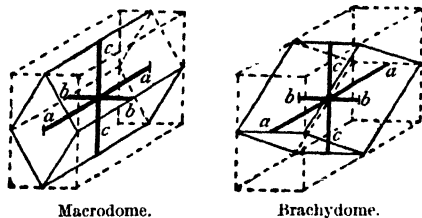


FIG. 197.—Dome and pinakoid faces.

pinakoids of the brachy-axis. These are the diamond-shaped end faces in Fig. 197. In Fig. 198 (representing a crystal of barytes BaSO_4) the faces marked 010 constitute a macropinakoid, in this case a **basal pinakoid**; the faces 101 are **macrodomes**. The faces belonging to the prism form are marked 001. This notation is explained later.

(5) In the **monoclinic system** there are *three axes of different lengths, two intersecting at an oblique angle, whilst the third is at right angles to the plane of the other two* (Fig. 196 V.). Pyramid and prism forms, pinakoids and domes occur. The vertical axis is denoted by c ; the b -axis or **ortho-axis** is at right angles to the vertical axis, whilst the inclined or a -axis is the **clino-axis**. The angle between the vertical axis and clino-axis is called the **angle β** .

(6) In the **triclinic system** there are *three unequal axes intersecting one another obliquely* (Fig. 196 VI.). One of these is selected as the vertical axis, the other two are the macro-axis (longer) and the brachy-axis (shorter). The three angles between the axes are α, β, γ .

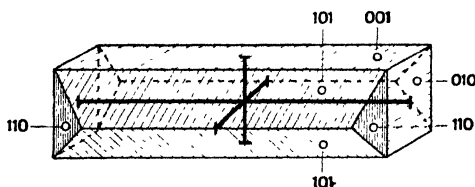


FIG. 198.—Barytes crystal.

Sometimes the rhombohedral system is taken as a seventh separate crystal system, but it is here regarded as containing hemihedral forms (see below) derived from the hexagonal system by suppressing half the faces. If all such derived forms were put into separate classes, the 32 symmetry groups (p. 357) would be obtained.

Most minerals belong to the monoclinic or rhombic systems; of 565 minerals listed by Beekenkamp, 186 were monoclinic, 155 rhombic, 85 regular, 51 rhombohedral, 36 triclinic, 32 tetragonal and 20 hexagonal.

Hemihedral forms.—Those forms in any system which have the full number of faces required by the symmetry of the system are called **holohedral forms**. If only half this number of faces are present, the form is known as **hemihedral**. Forms having only one quarter the full number of faces required by the symmetry of the system are called **tetartohedral**. (In the modern classification into symmetry groups, these are holohedral forms in separate classes.)

A hemihedral form is produced by suppressing half the faces of the holohedral form and producing the remainder to meet in new edges:

Fig. 199 shows the form obtained by producing alternate faces of the regular octahedron: it is the regular tetrahedron, having the four faces instead of eight. The tetrahedron is the hemihedral form of the octahedron.

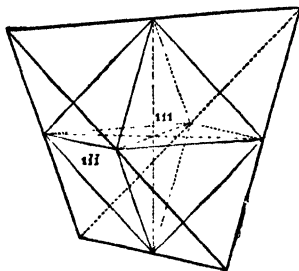


FIG. 199.—Relation of tetrahedron (hemihedral form) to octahedron (holohedral form).

Important hemihedral forms occur in the hexagonal system. By developing alternate faces of the hexagonal pyramid (Fig. 200) the positive or the negative rhombohedron (Fig. 201) is obtained. From the dihexagonal pyramid with 24 faces, obtained by the combination of two hexagonal pyramids, two kinds of hemihedral forms are produced: (i) suppressing alternate pairs of faces (Fig. 202) gives the scalenohedron (Fig. 203); (ii) suppressing alternate faces (Fig. 204) gives the trapezohedron (Fig. 205).

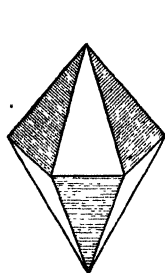
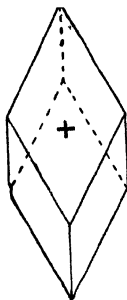
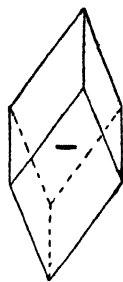


FIG. 200.
Hexagonal
pyramid.



Positive
rhombohedron.



Negative
rhombohedron.

The peculiar zig-zag form of the lateral edges of the scalenohedron and the trapezohedron will be observed, whilst the corresponding edges of the holohedral forms lie in a plane. Positive and negative hemihedral and also tetartohedral forms occur, which are not considered here.

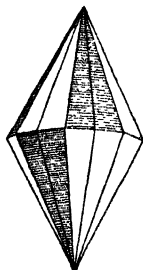


FIG. 202.
Dihexagonal
pyramid.

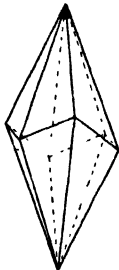


FIG. 203.
Scalenohedron.

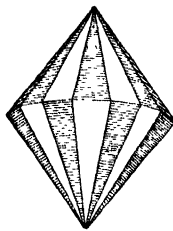


FIG. 204.
Dihexagonal
pyramid.

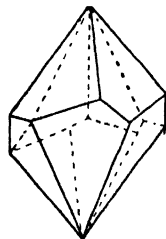
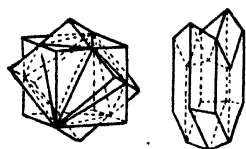


FIG. 205.
Trapezohedron.

Many of these forms occur in natural crystals of calcite (CaCO_3), and sometimes in twin crystals (p. 356), so that they often differ completely in appearance.

Twin crystals.—Two or more individual crystals may grow in contact so that neither is complete, and twin crystals (Fig. 206) are formed. The two crystals may coalesce except for a few faces, as in Fig. 207.



Fluorspar. Gypsum.
Fig. 206.—Twin crystals.

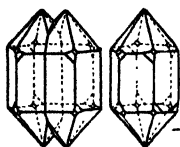


Fig. 207.—Twins of right- and left-handed quartz. Partial and complete interpenetration.

in a triclinic crystal) they will be oblique, and the angles $YOZ = \alpha$, $XOZ = \beta$ and $XOY = \gamma$ will not be right angles. Each prism face cuts one axis only, since it is parallel to the other two, and the intercepts are the distances a , b and c from O . If we imagine the face o extended in all directions it will intercept all three axes: whatever the size of o its intercepts will remain in the same ratios. These ratios, generally denoted by $a : b : c$ for the intercepts on the x , y and z axes, were called by Weiss (1818) the **parametral ratios**, the face o being the **parametral plane**. For the other pyramidal faces the parametral ratios are $a : -b : c$, $a : b : -c$ and $a : -b : -c$.

In all cases (whether the axes are rectangular or inclined) it is found that if o is an actual crystal face, the intercepts of any other actual face on the crystal can be expressed by the ratios $ma : nb : pc$, where m , n , p are either small rational numbers or infinity. For example, the prism face b makes intercepts $\infty a : lb : \infty c$, since it is parallel to OX and OZ and its intercepts are infinite, whilst it cuts OY at a point which may be taken as the intercept of a face (shown dotted as the triangle ABC) parallel to o . This law of rational intercepts was implied

in the attempts of Haüy since 1781 (*Essai d'une Théorie sur la Structure des Crystaux*, 1784) to show that derived forms may be produced by the decrements of successive layers of what he called *integrant molecules*, the form of which is that of the cleavage figure. The forms of rock-salt, for example, are produced by packing the hypothetical cubic integrant molecules together, and the development of an octahedral face ABC is shown in Fig. 209.

Haüy's idea was developed mathematically by Bravais (1848), who also recognised the relation between the arrangement of the particles and the cleavage of a crystal. He replaced the idea of a packing of integrant

Crystallographic notation.—The form shown in Fig. 208 contains two sets of faces, the set a , b , c and the face o . Through the centre O draw axes OX , OY , OZ parallel to the faces. These are the **crystallographic axes**. In the general case (for a tri-

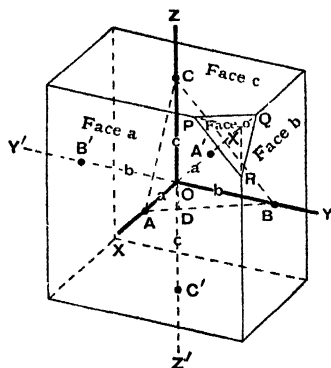


Fig. 208.—Crystallographic axes.

molecules by a structure in which the ultimate particles, which are considered as spheres in contact, are arranged in a **space lattice**, of which he recognised 14 types. By considering the grouping of points (representing the centres of atoms) in space lattices (Fig. 210), it has been shown that there are 230 generalised types, such that the assemblage around any selected point is the same as, or the mirror-image of, the assemblage around any other point in the lattice. These 230 types may be allocated to classes according to symmetry. It is found mathematically that there are 31 possible combinations of the elements of symmetry in crystals obeying the law of rational intercepts, so that if we add the case where there are no elements of symmetry, we obtain 32 **symmetry groups**. Of these, eleven include nearly all the common crystalline substances. The question as to what particles occupy the lattice points can now be decided, in principle, by X-ray analysis.

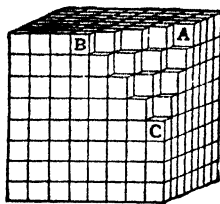


FIG. 209.—Integrant molecules according to Hauy.

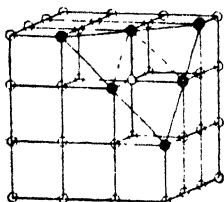


FIG. 210.—Space Lattice of sodium chloride.

in a bracket are the **Miller indices** of the face: (010) for the face *b* and (111) for the face *o* in Fig. 208. In the case of negative indices the sign is placed over the index: ($\bar{1}\bar{1}\bar{1}$).

As an example, consider the triclinic potassium dichromate crystal in Fig. 211. The edges selected for the directions of the three crystallographic axes *OX*, *OY*, *OZ* are the intersections of the faces *B* and *C*, *C* and *A*, and *A* and *B*, respectively. Hence the faces *A*, *B* and *C* will have the indices (100), (010) and (001) respectively. The parametral face chosen, giving the basic ratio $a : b : c$, is p , and since it cuts the axis *OZ* at its negative end, its indices will be ($\bar{1}\bar{1}\bar{1}$). The ratios $a : b : c$ and the angles α , β , γ between the axes ($\alpha = \angle YOZ$; $\beta = \angle XOZ$; $\gamma = \angle XOY$) are calculated from the different angles which these four faces *A*, *B*, *C* and *p*, make with one another. They are $a : b : c = 1.0116 : 1 : 1.8416$;

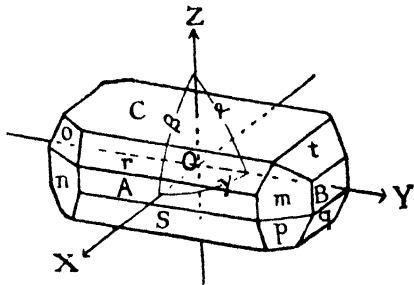


FIG. 211.—Potassium dichromate crystal.

$\alpha = 98^\circ 0'$, $\beta = 96^\circ 13'$, $\gamma = 90^\circ 51'$. (It is customary to put the *b* axis ratio equal to unity, the ratios for the *a* and *c* axes being adjusted to correspond with this). The indices of the remaining faces are

then found to be (as they are lettered in the figure): $s(10\bar{1})$, $r(101)$, $m(110)$, $n(1\bar{1}0)$, $q(0\bar{1}1)$, $t(012)$, $o(1\bar{1}1)$, obeying the law of rational intercepts.

ISOMORPHISM.

Isomorphism.—The Abbé Haüy (1743–1822), the founder of crystallography, laid down as fundamental axioms that: (i) *identity of crystalline form* (except in the regular system) *implies identity of chemical composition*; and conversely (ii) *difference in crystalline form implies difference in chemical composition*.

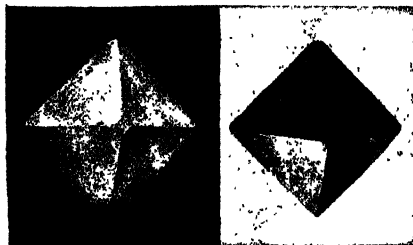
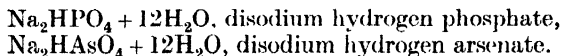


FIG. 212.—Crystals of common alum (left) and chrome alum (right).

Exceptions were known. Klaproth (1788) showed that calcium carbonate crystallises in the hexagonal form as calcite and in the rhombic form as aragonite. Romé de l'Isle (1772) observed that copper sulphate and ferrous sulphate crystallise from mixed solu-

tions in the form of the latter. The alums have the same crystalline form but differ in chemical composition (Fig. 212).

Mitscherlich (1819) showed that phosphates and arsenates of similar composition and containing the same amount of water of crystallisation, have almost exactly the same crystalline form:



In the case of $\text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$ and $\text{NaH}_2\text{AsO}_4 + \text{H}_2\text{O}$ the ordinary crystalline forms differ, but the phosphate sometimes crystallises in a form identical with the common form of the arsenate.

Mitscherlich pointed out that the existence of rhombic and monoclinic sulphur shows that elements may have different crystalline forms. One substance (element or compound) may have two distinct crystalline forms, and is then called **dimorphous**. If it has more than two forms it is called **polymorphous**.

The capacity of different substances of crystallising in the same form, Mitscherlich called **isomorphism**; substances crystallising in the same form are **isomorphous**. Since many analogous compounds of phosphorus and arsenic are isomorphous, the name was applied to the elements themselves. **Isomorphous elements** form similarly crystallising compounds with the same elements or radicals, and can replace one another in compounds without essential alteration in crystalline form. (It is not necessary that the *free* elements shall have similar crystalline forms, although this may be the case.)

Mitscherlich at first thought that the same number of atoms combined in the same manner produce the same crystalline form, no matter what is the chemical nature of the atoms. This generalisation was afterwards limited to the statement that an atom can be replaced by another without producing a change of form only when the elements are alike chemically.

Accurate measurements of crystal angles showed, as Mitscherlich conjectured, that the law is only approximate. In 1812 Wollaston had found with the reflecting goniometer that the corresponding angles in calcite, dolomite, and spathic iron ore are $74^{\circ} 55'$, $73^{\circ} 45'$, and $73^{\circ} 0'$. Except in the regular system, the replacement of an atom by an atom of an isomorphous element leads to a change in crystal angles which may be small but may be several degrees. Haüy's first axiom is therefore correct in the strictest sense.

Tutton (1893-1925) found that the crystal angles in isomorphous sulphates and selenates of potassium, rubidium, and caesium change slightly when one isomorphous element (K, Rb, Cs, or S, Se) is replaced by another. The change, expressed in terms of the ratios of the lengths of the axes a , b , c , depends in a regular manner on the atomic weight of the element :

K_2SO_4	$a : b : c = 0.5727 : 1 : 0.7418$
Rb_2SO_4	$a : b : c = 0.5723 : 1 : 0.7485$
Cs_2SO_4	$a : b : c = 0.5712 : 1 : 0.7531$
$(NH_4)_2SO_4$	$a : b : c = 0.5635 : 1 : 0.7319$

The other properties (molecular volume, refractive indices, coefficients of expansion, thermal conductivity) alter with the crystal angles, showing that the form is closely related to the nature of the atoms in the crystal.

Isomorphous elements.—It is possible to classify the elements into groups, the members of each group, capable of replacing one another without sensible alteration of crystalline form, being called **isomorphous elements**.

- I. Cl, Br, I, F ; Mn (in permanganates, *e.g.* $KMnO_4$ isomorphous with $KClO_4$).
- II. S, Se ; Te (in tellurides) ; Cr, Mn, Te (in the compounds K_2RO_4) ; As and Sb in the glances MR_2 .
- III. As, Sb, Bi ; Te (element) ; P, V (in salts) ; N, P (in organic bases).
- IV. K, Na, Cs, Rb, Li ; Tl, Ag.
V. Ca, Sr, Ba, Pb ; Fe, Zn, Mn, Mg ; Ni, Co, Cu ; Ce, La, Pr, Nd ; Er, Y with Ca ; Cu, Hg with Pb ; Cd, Be, In with Zn ; Tl with Pb.
- VI. Al, Fe, Cr, Mn ; Ce, U in oxides R_2O_3 .
- VII. Cu, Ag in lower oxides ; Au.
- VIII. Pt, Ir, Pd, Rh, Ru, Os ; Au, Fe, Ni ; Sn, Te.
- IX. C, Si, Ti, Zr, Th, Sn ; Fe, Ti.
- X. Ta, Nb.
- XI. Mo, W ; Cr.

Several elements occur in more than one group. Chromium occurs in VI with Al, Fe, etc. because of the isomorphism of the oxides R_2O_3 , the spinels, RR'_2O_4 , *e.g.* $MgAl_2O_4$, $FeFe_2O_4$, $FeCr_2O_4$, etc., and the alums, *e.g.* $KAl(SO_4)_2 \cdot 12H_2O$, $KCr(SO_4)_2 \cdot 12H_2O$, $KFe(SO_4)_2 \cdot 12H_2O$. It occurs in

group II because of the isomorphism of the salts K_2SO_4 , K_2CrO_4 , K_2MnO_4 , etc. Manganese occurs in group V because of the isomorphism of the carbonates $CaCO_3$, $FeCO_3$, $MnCO_3$; in group VI because of the isomorphism of the spinels (containing trivalent Mn, Fe, etc.); in group II because of the isomorphism of K_2MnO_4 with K_2SO_4 , etc.; and in group I because of the isomorphism of $KMnO_4$ and $KClO_4$. The relation between the valencies and the positions in the groups is clear.

Atomic weights from isomorphism.—The application of isomorphism to the deduction of atomic weights is based on the axiom that *isomorphous compounds have similar formulae*.

Potassium selenate crystallises in the same form as potassium sulphate, hence Mitscherlich concluded that its formula is K_2SeO_4 , corresponding with K_2SO_4 . From its composition the atomic weight of selenium could then be calculated. Ferric oxide, chromic oxide, and alumina are isomorphous. The vapour density of aluminium chloride corresponds with the formula $AlCl_3$. The formula of alumina will then be Al_2O_3 . We assume the formulae Fe_2O_3 for ferric oxide and Cr_2O_3 for chromic oxide, and from the compositions of the oxides the atomic weights of the metals may be calculated. These are confirmed by the specific heats, which are 0.1096 and 0.104 respectively.

A good example of isomorphism is that studied by Roscoe in fixing the atomic weight of vanadium. The following minerals had the formulae given in the second column assigned to them by Berzelius:

Apatite,	$3Ca_3(PO_4)_2 + CaF_2$.	$3Ca_3(PO_4)_2 + CaF_2$.
Pyromorphite,	$3Pb_3(PO_4)_2 + PbCl_2$.	$3Pb_3(PO_4)_2 + PbCl_2$.
Mimetite	$3Pb_3(AsO_4)_2 + PbCl_2$.	$3Pb_3(AsO_4)_2 + PbCl_2$.
Vanadinite,	$3Pb_3V_2O_6 + PbCl_2$.	$3Pb_3(VO_4)_2 + PbCl_2$.

In these lead and calcium, and arsenic and phosphorus, replace each other, but the formula of vanadinite is different from those of the other compounds, although the minerals crystallise in the same form. Roscoe concluded that Berzelius had given the wrong formula to vanadinite.

By reinvestigating vanadium compounds Roscoe was able to show that what was regarded as metallic vanadium by Berzelius was really an oxide VO. The formulae of the minerals, as shown in the third column, were then analogous. The atomic weight of vanadium found by Berzelius, 68.5, was the molecular weight of VO, and the true value was $68.5 \cdot 16 : 52.5$. Roscoe found that the actual vanadium compounds used by Berzelius contained phosphoric acid, which is difficult to separate. By using pure compounds he found $V = 51.4$.

The minerals are now formulated as $Ca_5F(PO_4)_3$, $Pb_5Cl(PO_4)_3$, $Pb_5Cl(AsO_4)_3$, and $Pb_5Cl(VO_4)_3$.

Formulae of minerals.—Since one element can partly replace an equivalent amount of an isomorphous element in a compound, the formula of the compound will not usually give a whole number of atoms of each isomorphous element. Spathic iron ore $FeCO_3$ may have the iron partly replaced by isomorphous manganese. The proportions of the two metals may vary from Fe - 48.2 per cent and Mn - 0, to Fe - 0 and Mn = 47.8 per cent.

Such an **isomorphous mixture** is represented by a formula such as $(\text{Fe}, \text{Mn})\text{CO}_3$, the isomorphous elements enclosed in brackets behaving as an equivalent amount of one element. The sum of the *atomic* proportions of Fe and Mn combined with CO_3 , must always be unity.

Solid solutions.—Isomorphous substances may crystallise together from solution to form *homogeneous* crystals containing them in variable proportions. These are called **mixed crystals**, but a better name is **solid solutions**. These are also formed from a fused state.

If chrome alum $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and ordinary potash alum $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, which form deep purple and colourless octahedral crystals respectively, are dissolved together in water and the solution crystallised, octahedral crystals containing both alums separate, with colours varying from pale to deep purple according to the amount of chrome alum. Substances which crystallise in the same form but belong to different chemical types do not form mixed crystals, or only to a limited extent, whereas chemically analogous compounds may form mixed crystals even though the crystal angles differ as much as 5°, the resulting crystals having angles between those of the components.

Retgers (1889) considered the property of forming mixed crystals an important criterion of isomorphism, also that the variation in the physical properties of the mixed crystal with the proportion of its constituents is a guide in deciding if the substances are truly isomorphous. If the specific volume, *i.e.* the reciprocal of the density, is plotted against the proportions of the constituents, the points must, according to Retgers, lie on a straight line which shows no change of direction. The substances may be only partly miscible, in which case there is a gap in the line, but if they are isomorphous one part of the line is a continuation of the other.

There are many exceptions to Retgers's theory. Potassium and sodium chlorides crystallise in the same form and have identical lattices but do not form mixed crystals. The capacity for forming mixed crystals seems to depend on approximate equality of the volumes of the structural units. Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, molecular volume (m.v.) 74, mixes in all proportions with rubidium sulphate Rb_2SO_4 , m.v. 73, with potassium sulphate K_2SO_4 , m.v. 65, and caesium sulphate Cs_2SO_4 , m.v. 85, whilst potassium and caesium sulphates are completely immiscible, although they are isomorphous.

Overgrowth crystals.—If an octahedral crystal of chrome alum is suspended by a thread in a saturated solution of potash alum, a colourless overgrowth of potash alum is deposited on the violet crystal of chrome alum as a nucleus. A green crystal of nickel sulphate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ may be covered with colourless zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Kopp (1879) regarded the property of forming overgrowth crystals as characteristic of isomorphous substances, but exceptions are known; rhombic (pseudohexagonal) K_2SO_4 may form an overgrowth of hexagonal KNaSO_4 .

Apparent exceptions to the law of isomorphism.—Apparent exceptions to the law of isomorphism are frequent. They are sometimes due to the existence of two or more varieties of a substance—**dimorphism** or

polymorphism respectively—only one of which, not the common form, is isomorphous with the common variety of a chemically similar substance. An example of this was discovered by Mitscherlich, viz. the acid phosphate and the acid arsenate of sodium, one form being rhombic and the other monoclinic: $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$.

In many cases isomorphism is found with chemically similar substances with different numbers of atoms in the molecule: ammonium salts containing the radical NH_4 are isomorphous with potassium and sodium salts containing the atoms K and Na: silver sulphide Ag_2S in the mineral *argentite* is isomorphous with lead sulphide PbS in *galena*, the two forming mixed crystals. In other cases, compounds which have the same numbers of atoms in the molecule but are not chemically analogous are isomorphous: calcium carbonate CaCO_3 occurs in the same form (*calcite*) as sodium nitrate NaNO_3 , and Mg_2SiO_4 and Al_2BeO_4 are isomorphous. Crystals of sodium nitrate form parallel growths on calcite crystals.

Other examples of this type of isomorphism are shown in the following groups:

- | | |
|------------------------------------------------|---------------------------------------------|
| (1) Potassium periodate KIO_4 | (3) Potassium perchlorate KClO_4 |
| Calcium tungstate CaWO_4 | Barium sulphate BaSO_4 |
| Potassium osmiumate KOsO_3N | Potassium fluoborate KBF_4 |
| (2) Potassium sulphate K_2SO_4 | (4) Yttrium phosphate YPO_4 |
| Potassium beryllium fluoride | Zircon ZrSiO_4 |
| K_2BeF_4 | Tinstone SnO_2 or SnSnO_2 |

In these groups the molecules contain the same number of atoms, and the original idea of Mitscherlich that the form depends on the number of atoms and not on their chemical nature, seems to be verified.

These apparent exceptions to the law of isomorphism receive an explanation from the results of X-ray investigations and the modern theory of atomic structure, as explained in Chapter XXIII.

The X-ray examination of mixed crystals (solid solutions) has shown that they give a diagram very like that of both components and not a superposition of the diagrams of the two. The replacement of one atom by another in the mixed crystal is random, and in the case of alloys a uniform distribution is attained only after prolonged annealing, when the atoms change places. It was found by Vegard (1921) that the length of side of the cubic lattice (Fig. 210) of a mixed crystal of potassium chloride and potassium bromide is given by the linear relation:

$$a_m = a_{\text{KBr}}(p - 100)/100 + a_{\text{KCl}}p/100$$

where p is the molar percentage of KCl in the crystal and a_{KBr} and a_{KCl} are the lengths of the sides of the potassium bromide and potassium chloride lattices.

Ionic size and crystal structure.—In a lattice formed of two types of atoms or ions A and B, the number of atoms of B arranged around any given atom of A is called the *crystallographic coordination number* of A (not to be confused with the coordination number in Werner's theory of coordination compounds, p. 417). It depends on the radii of A and B, large atoms or

ions permitting a greater number of ions or atoms to pack around them than is the case with smaller particles. If r_1 and r_2 are the radii of A and B, the extreme ratios of the radii for various coordination numbers are :

Coordination number	3	4	6	8	12
Ratio r_1/r_2	0.15	0.225	0.414	0.732	1.000

The coordination numbers 5, 7, 9, 10 and 11 are excluded by geometry if the ionic charges are to balance. For a particular ion the coordination number may vary with the other ion, owing to the polarising action (p. 442).

Elements of similar ionic radii and preferably, though not necessarily, of the same ionic charge, can replace one another in solids ; if the radii are similar but the charges different, adjustment may occur in the lattice, and an ion of greater charge is more readily included than one of smaller charge. This explains why some elements usually occur together in minerals, and why, for example, in the crystallisation of magnesium minerals scandium occurs in the first crystals and lithium in the last.

around a vertical cylinder, divided into sixteen vertical strips, and found that similar elements fell on the same vertical. The "De Chancourtois helix" was a precursor of the Periodic Law.

Newlands in 1864 said that if the elements are arranged in *the order of atomic weights*, "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music," and he called this the **law of octaves** :

1 H	2 Li	3 Be	4 B	5 C	6 N	7 O
8 F	9 Na	10 Mg	11 Al	12 Si	13 P	14 S
15 Cl	16 K	17 Ca	19 Cr	18 Ti	20 Mn	21 Fe, etc.

This is based on what are now called the **atomic numbers** of the elements, but was not very satisfactory since manganese, for example, does not resemble phosphorus. Newlands pointed out that regularities appear only when the atomic weights derived systematically by Cannizzaro (p. 108) are used, and his table contains the germ of the Periodic Law.

The periodic law.—The periodic law, which is the basis of the modern system of classification of the elements, was put forward independently in 1869 by Mendeléeff in Russia and in 1870 by Lothar Meyer in Germany. (Odling in 1865 had arranged the elements in a table which resembles Mendeléeff's table of 1869.)

Mendeléeff says his basic idea was that "there must be some bond of union between mass and the chemical elements; and as the mass of a substance is ultimately expressed in the atom, a functional dependence should exist and be discoverable between the individual properties of the elements and their atomic weights. But nothing, from mushrooms to scientific dependence, can be discovered without looking and trying. So I began to look about and write down the elements with their atomic weights and typical properties, analogous elements, and like atomic weights on separate cards, and this soon convinced me that *the properties of the elements are in periodic dependence upon their atomic weights*; and although I have had my doubts about some obscure points, yet I have never once doubted the universality of this law, because it could not possibly be the result of chance."

The original statement of Mendeléeff (1869) includes practically the whole content of the Periodic Law. It is given in eight paragraphs :

(1) The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

(2) Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (platinum, iridium, osmium), or which increase regularly (potassium, rubidium, caesium).

(3) The arrangement of the elements, or of groups of elements, in the order of their atomic weights, corresponds with their so-called *valencies*.

(4) The elements which are the most widely distributed in nature have *small* atomic weights, and . . . sharply defined properties. They are therefore *typical elements*.

* (5) The *magnitude* of the atomic weight determines the character of an element [and those of its compounds].

(6) The discovery of many yet unknown elements may be expected, for instance, elements analogous to aluminium and silicon, whose atomic weights would be between 65 and 75.

(7) The atomic weight of an element may sometimes be corrected by the aid of a knowledge of those of the adjacent elements.

(8) Certain characteristic properties of the elements can be foretold from their atomic weights.



D. I. MENDELÉEFF (1834-1907).

The periodic table.—Mendeléeff arranged the elements in a table called the periodic table, a modern form of which is given on p. 368. In this the elements are arranged in nine vertical columns called **groups**, headed by zero (0) and the Roman numerals from I to VIII, or (as in the table given) the zero group is made a **sub-group** of VIII, each group being subdivided into *a* and *b* as shown. These groups are formed by suitably **breaking up** into **periods** a continuous series of the elements arranged in the order of their atomic weights. The ordinal numbers, called **atomic numbers**, and not the atomic weights, are given in the table.

If the periods are written one under the other in horizontal rows, the vertical columns are the groups.

The first period contains two elements, hydrogen and helium ; each of the next two periods contains eight elements. The elements of the third period are analogous to those vertically above them in the second period. In other words, *the properties of successive elements in an earlier period recur in the same order in a later period.* This is seen in the two periods :

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	A

Lithium and sodium, for example, are alkali metals which decompose water in the cold ; fluorine and chlorine are gases which combine very readily with metals and form similar salts, and so on. The first three periods, from hydrogen to argon, are called **short periods**. (Formerly the second and third periods were called "the first two short periods", but this name is now unsuitable).

SHORT PERIODIC TABLE

PERIOD.	SERIES.	GROUP.																
		I.		II.		III.		IV.		V.		VI.		VII.		VIII.		(0)
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	b
1	1	H 1																He 2
2	2	Li 3	Be 4			B 5	C 6			N 7	O 8			F 9				Ne 10
3	3	Na 11	Mg 12			Al 13	Si 14			P 15	S 16			Cl 17				A 18
4	4	K 19	Ca 20	Sc 21		Ti 22	V 23			Cr 24	Mn 25	Fe 26	Co 27	Ni 28				Kr 36
	5		Cu 29	Zn 30		Ga 31	Ge 32	As 33		Se 34	Br 35							
5	6	Rb 37	Sr 38	Y 39		Zr 40	Nb 41			Mo 42	Tc 43	Ru 44	Rh 45	Pd 46				Xe 54
	7		Ag 47	Cd 48		In 49	Sn 50	Sb 51		Te 52	I 53							
6	8	Cs 55	Ba 56	Rare Earths 57-71		Hf 72	Ta 73			W 74	Re 75	Os 76	Ir 77	Pt 78				Rn 86
	9		Au 79	Hg 80		Tl 81	Pb 82	Bi 83		Po 84	At 85							
7	10	Fr 87	Ra 88	Ac 89		Th 90	Pa 91			U 92								

After argon ten elements instead of eight are passed over before the periodic recurrence of properties begins again with copper, and a close analogy, *e.g.* that between rubidium and potassium, only after eighteen elements.

At the beginning of the fourth period we meet with a difficulty. The element next in order of atomic weight to chlorine is potassium, which undoubtedly belongs to the same group as sodium. The next element

is argon, which is an inert gas resembling helium and neon and therefore belongs to the zero, or VIII *b*, group. The order of atomic weights of potassium and argon is the reverse of the order in the periodic system which brings them into the same groups as their chemical analogues.

In such cases, where the atomic weights are apparently inverted, the elements are put in the groups to which they naturally belong. Three such pairs of common elements are :

1. A 40, K 39 2. Co 59, Ni 58.7 3. Te 127.6, I 126.92

and another case is believed to occur in the last period of radioactive elements, viz. thorium (Th) 232 and protoactinium (Pa) 230. These supposed anomalies are now easily explained, since the elements concerned are mixtures of isotopes (p. 382).

With this transposition of argon and potassium, the natural sequence runs along the period until manganese is reached. We then expect an inert element resembling argon. Actually we find three elements, iron, cobalt and nickel, with almost identical atomic weights and very similar physical and chemical properties. After these three elements come copper, zinc, etc., which resemble in some respects the elements of Groups I, II, etc., and the inactive element does not appear.

The three elements iron, cobalt and nickel are placed in a separate group, viz. Group VIII *a*, no representatives of which are found in earlier periods. The elements following, viz. copper, zinc, etc., which do not closely resemble the earlier elements of the same groups, are separated from these by placing them on the right or in *b* positions in the groups, whilst the other elements are placed on the left or in *a* positions.

The elements in Group VIII *a* are called **transitional elements**, and instead of two **short periods** each of eight elements, the whole 18 elements from potassium to krypton inclusive form a **long period**, divided into elements belonging to **even** and **odd series** according as they occur in series of even (*e.g.* K) or odd (*e.g.* Cu) number, beginning with hydrogen.

This first long period is followed after krypton by a second long period beginning with rubidium, followed by the even elements of the period as far as molybdenum. These resemble the corresponding even elements of the preceding long period. After molybdenum comes an "artificial element" (p. 405) called technetium (since the discovery of "masurium" in 1925 does not seem to have been substantiated), followed by a cluster of three elements with very similar atomic weights and physical and chemical properties, viz. ruthenium, rhodium and palladium. These are obviously transitional elements of the same type as iron, cobalt and nickel, and must be placed in Group VIII *a*. The odd elements of the long period then follow, ending with xenon.

Near the end of this period is a repetition of the inversion of atomic weights met with in argon and potassium. Iodine is a halogen belonging to Group VII, whilst tellurium is an element of Group VI which contains its analogues sulphur and selenium. In the order of atomic weights the positions would be reversed. Again the two elements are placed in those positions which agree with their chemical properties.

A new period begins with caesium and proceeds as far as lanthanum in Group III in a regular manner. Lanthanum begins a series of fifteen elements with atomic weights differing by one, two, or even four units, all of which are most closely analogous in chemical properties and very difficult to separate in analysis. These, with scandium and yttrium in previous periods, are the elements of the **rare earths** (No. 61 is an artificial element called promethium, as the existence of a previously described "illinium" has not been substantiated). It is impossible to proceed to the normal manner with the rare-earth elements Nos. 57 to 71.

In this case, instead of one element occupying one place in the group there seems to be a cluster of fifteen. These must be placed in the same group as scandium and yttrium, so that the regular change in properties of the elements is checked at this point and goes forward again only when the atomic weight has increased by about 40 units. Then after lutecium, the last rare-earth element, comes the element hafnium discovered in zirconium minerals by Coster and Hevesy in 1923. It occupies the position in Group IV previously given to cerium, which is now placed in Group III with the other rare-earth elements.

After hafnium come tantalum, tungsten, rhenium, and finally the three transitional elements osmium, iridium and platinum, which fall in Group VIII *a*. The rest of this long period continues from gold in Group I to bismuth in Group V and the radioactive element polonium in Group VI. Element No. 85 in Group VII is the artificial element astatine. The period closes with the inert radioactive gas radon in Group VIII *b* (or Group O). This long period contains in all 32 elements.

The numbers of elements in the periods up to this point are 2, 8, 8, 18, 18, and 32. A new period begins with the newly discovered radioactive element francium in Group I, and continues as far as uranium, all the elements in this group being strongly radioactive. We should expect many more elements in this period, and a few elements of atomic weights higher than uranium (the **transuranic elements**) have been obtained artificially (p. 407) and all are radioactive. They are not included in the present table, since their group assignments are still uncertain.

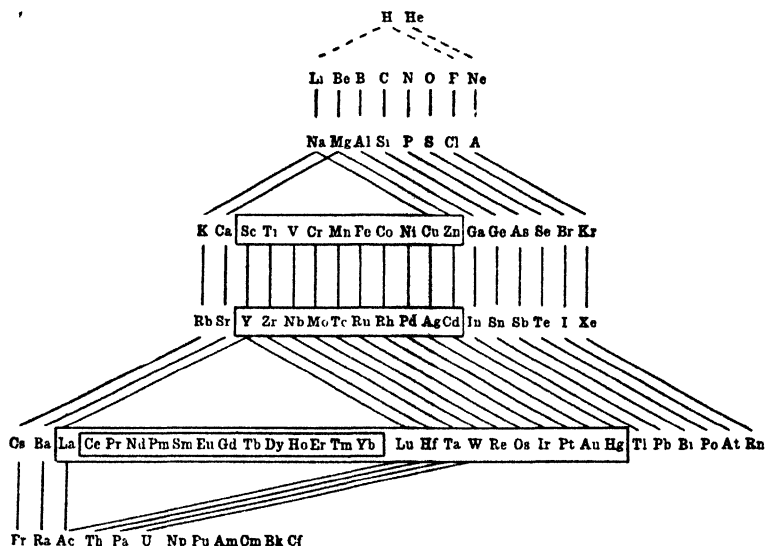
Although the short form of the Periodic Table (due to Lothar Meyer) which is given on p. 368, is most convenient for elementary students and for general use, and corresponds with the short table of atomic structures given on p. 411, some prefer the so-called *Long Periodic Table* (originating with Mendeléeff) a modified form of which is given on p. 371.

This corresponds with a fuller table of atomic structures. The rectangles enclose elements with incomplete *inner* shells of electrons in the atoms, which are called "transitional elements" in the wider sense, the **rare earths** (except scandium and yttrium) taking their place inside a larger period of transitional elements. The double relation of hydrogen to Groups I and VII is also seen.

The periodicity of valency.—Mendeléeff pointed out that the number of a group corresponds with the valency of the elements in it. In some

cases (P, S, Cl, Cr, Mn) it is necessary to take the maximum valency, in others (Cu, Ag, Au) the minimum valency, and the assignment of valency seems a little artificial, as Wyruboff (1896) said, but the

LONG PERIODIC TABLE



reason is now fairly clear from the point of view of atomic structure. The valencies are clearly seen with the fluorine and oxygen compounds :

I	II	III	IV	V	VI	VII	VIII
NaF	CaF ₂	BF ₃	SiF ₄	PF ₅	SF ₆	IF ₇	OsF ₈
Na ₂ O	CaO	B ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Mn ₂ O ₇	OsO ₄

Lothar Meyer's curve.—The periodicity of properties with increase in atomic weight (or atomic number) is strikingly shown (Fig. 213) in the **atomic volume curve** of Lothar Meyer, in which the atomic volumes (volumes in ml. occupied by the atomic weight in grams. = at. wt. *A* divided by density *D*) are plotted against the atomic numbers, *i.e.* the ordinal numbers of the elements in the periodic table. The atomic volumes rise and fall in a periodic manner. The alkali metals, the atoms of which are unusually bulky, are at the peaks of the curve.

The atomic volumes represent, not the space occupied by the atoms themselves, but this plus the empty spaces between. If the atoms are assumed to be spherical and in contact, $\sqrt[3]{A/D}$ is a measure of the **mean distance** between the atomic centres.

The atomic volumes of a few important elements are given below.

Element.	Atomic volume at 15°.	Element.	Atomic volume at 15°.
Hydrogen	- 13.2 (at - 250°)	Strontium	- 34.5
Lithium	- 13.0	Barium	- 36.2
Sodium	- 23.7	Chlorine	- 20.6 (liq. at 0°)
Potassium	- 45.5	Bromine	- 25.4
Rubidium	- 56.25	Iodine	- 25.7
Caesium	- 70.6	Iron	- 7.10
Calcium	25.9	Lead	18.3

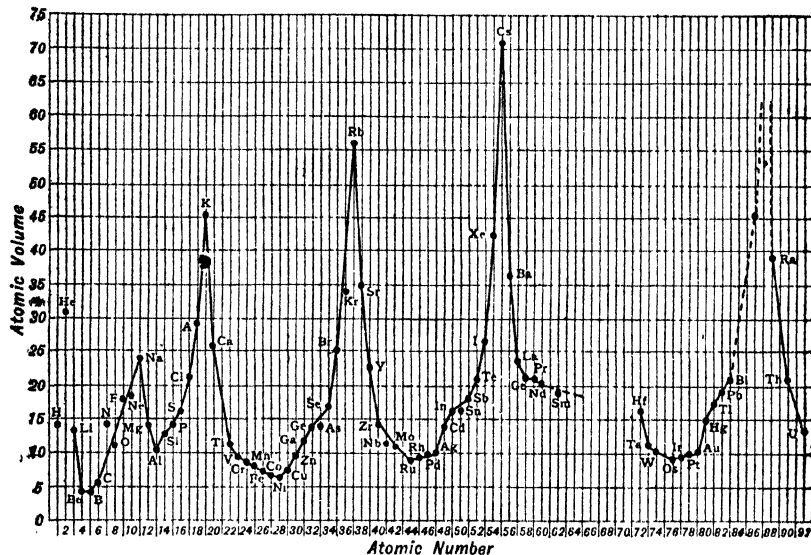


FIG. 213.—Lothar Meyer's atomic volume curve.

Mendeléeff remarked that reactive elements have large atomic volumes (alkali metals, halogens); elements which are not very reactive have small atomic volumes (C as diamond, Ni, Co, Ir, Pt).

The atomic volume curve also shows periodicity in other properties, such as expansion by heat, magnetic susceptibility, melting point, refractive index, boiling point, crystalline form, compressibility, atomic heat at low temperatures, heats of formation of oxides and chlorides, hardness, malleability, volatility, volume change on fusion, viscosity and colour of salts in solution, mobilities of ions, electrode potentials of metals, over-voltage of metals, frequency of atomic vibrations in solids, distribution of the elements in nature, distribution of lines in spectra, and valency.

Lothar Meyer pointed out that gaseous elements and those fusing below a red heat occur at the maxima and on ascending portions of the atomic volume curve. Difficultly fusible elements occur at the minima or on descending portions of the curve.

MELTING AND BOILING POINTS OF THE CHEMICAL ELEMENTS (in degrees C)

Element.	M. pt.	B. pt.	Element.	M. pt.	B. pt.	Element.	M. pt.	B. pt.
Aluminium	659.8	>2000	Iodine	113.9	184.4	Rhodium	1970	>2500
Antimony	630.5	1380	Iridium	2440	>4800	Rubidium	39.00	700
Argon	-189.2	-185.9	Iron	1539	2450	Ruthenium	2450?	>2700
Arsenic	81.4.5*	subl. 61.5	Krypton	-157	-152.9	Samarium	1350	—
Barium	710	1536	Lanthanum	327.4	1800	Scandium	1500	2400
Beryllium	1280	1500	Lead	180	1620	Selenium (grey)	220	685
Bismuth	271	1450	Lithium	180	1336	Silicon	1420	2600
Boron	2300	2550	Magnesium	651	1100	Silver	960.5	1955
Bromine	-7.2	58.8	Manganese	1260	1600	Sodium	97.90	882.9
Cadmium	320.9	767.3	Mercury	-38.87	356.9	Strontium	800	1366
Cæsium	28.45	670	Molybdenum	2630	3700	Sulphur	{S ₈ 112.8 S ₁₁₉₋₂₅	444.60
Calcium	851	1439	Neodymium	840?	—	Tantalum	2850	>4100
Carbon	3500	4200	Neon	-248.5	2900	Tellurium	449.8	1390
Cerium	640	1400	Nickel	1452	2900	Thallium	303.5	1475
Chlorine	101.6	-34.5	Niobium	1950	3700	Thorium	1845	>3000
Chromium	1840	>2900	Nitrogen	-210	-195.8	Tin	231.84	2260
Copper	1083.0	2310	Osmium	2750	>5300	Titanium	1800	>3000
Cobalt	1480	2900	Oxygen	-218.4	-183.0	Tungsten	3390	3500
Fluorine	-218	-187	Palladium	1553	2200	Uranium	1150	3500†
Gallium	29.75	>2000	Phosphorus	44.1	287	Vanadium	1710	3.00
Germanium	958	2700	Potassium	63.5	758	Xenon	-111.5	-107.1
Gold	1063.0	2610	Praseodymium	940	—	Yttrium	1475	2500
Hafnium	2200	3200	Radium	960	1140	Zinc	419.45	920
Helium	-272 +	-268.87	Rhenium	-71	-61.8	Zirconium	1600	2900
Hydrogen	-259.14	-252.76		3167	—			
Indium	155.4	>1450						

* At 36 atm. † At 23 atm.

Carnelly found a similar periodic dependence of the melting points of metallic chlorides, and the heats of formation of the oxides and chlorides, on the atomic weight of the metal; the periodicity of properties extends to the compounds of elements.

Electrochemical character.—The electrochemical character of an element is roughly defined by the chemical character of its oxide: **electropositive elements** yield *basic oxides*, **electronegative elements** yield *acidic oxides*. If the part of the atomic volume curve between two maxima is called a *section*, then all elements on descending parts of the second and third sections are electropositive; those on ascending portions are electronegative. Elements situated on sections 4 and 5 show electrochemical properties passing through two periods whilst the atomic volumes pass through only one.

On the first part of the descending curve of each of sections 4 and 5 strongly electropositive elements occur (K, Ca; Rb, Sr); followed on the same part of the curve by more or less electronegative elements (V, Cr, Mn; Zr, Nb, Mo, Ru, Rh), which are again followed on the ascending portions of the curve by electropositive elements (Fe, Ni, Co, Cu, Zn, Ga; Pd, Ag, Cd, In); finally, after these on the same but higher parts of the curve, come electronegative elements (As, Se, Br; Sn, Sb, Te, I).

Strongly electropositive elements associate towards the left of the table, beginning with Group I; strongly electronegative elements occur on the right of the table, the most marked being in Group VII. In passing along a period from Group I to Group VII the electropositive character diminishes. When Group IV is reached the elements show very little electrochemical character, either positive or negative, and are practically neutral. The electropositive character changes in Group V into electronegative, which becomes increasingly stronger and reaches a maximum in Group VII.

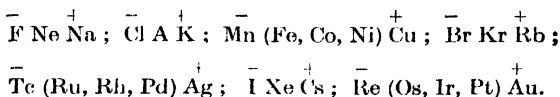
The electrochemical character is well shown in the oxides of elements of the third period:

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇
strongly basic	basic	weakly basic and acidic	weakly acidic	fairly strongly acidic	strongly acidic	very strongly acidic

The gradation of electrochemical character is also shown in the groups themselves. It is worthy of note that the non-metallic elements are confined to the upper right-hand part of the table.

The inert gases, which form no compounds and have zero valency, occupy the zero group or Group VIII *b*, separating the intensely electronegative elements of Group VII from the intensely electropositive elements of Group I. The transitional elements of Group VIII *a* perform this function for the three parts of long periods where there is no inactive element.

Here, however, the positive and negative properties of the elements in the first and seventh groups are much less marked than in the cases where inactive elements are interposed :



The last members of the even series resemble in many respects the first members of the next odd series (excluding the zero group). Thus, there is a gradual transition from chromium and manganese to copper and zinc, apart from the bridge formed by the transitional elements. This gradation of properties in the *periods* was insisted upon by Mendeléeff : the resemblances between Li and Mg, between Be and Al, and between B and C, are striking.

Gaseous Hydrides.—All elements occupying places 1 to 4 before an inert gas (and also boron) form gaseous hydrides. Elements in groups I to III α (except boron) give salt-like or other solid hydrides, such as NaH. Beryllium and magnesium do not form hydrides. The volatile hydrides are covalent compounds, but the solid hydrides conduct electricity when fused, the hydrogen behaving as an anion (Li^+H^-). A different group of hydrides are metallic hydrides CuH, Pd₂H and NiH₂. Silver hydride produced by the prolonged action of atomic hydrogen on silver foil, is said to be salt-like.

I	II	III	IV	V	VI	VII	VIII α	
Li	---	B	C	N	O	F	Ne	
Na	--	}	Si	P	S	Cl	A	
K	Ca		Al	Ge	As	Se	Br	Kr
Rb	Sr		Ga	Sn	Sb	Te	I	Xe
Cs	Ba		La	Pb	Bi	Po	—	Rn
		etc.						

Correction of atomic weights.—By fixing the positions of the elements in the periodic table, Mendeléeff was able to correct some atomic weights.

The metal beryllium, equivalent 4.5, seemed to resemble aluminium. The hydroxides are gelatinous precipitates soluble in acids and alkalis ; the normal carbonates cannot be prepared by precipitation, as they hydrolyse : the metals, obtained by electrolysis of the double potassium fluorides, dissolve in alkalis with liberation of hydrogen. The specific heat of beryllium pointed to 14.8 for the atomic weight. All these results seemed to make beryllium trivalent, the oxide being Be₂O₃, resembling Al₂O₃. But there is no place for an element of this atomic weight in the first period : B 11 C 12 N 14 O 16. Avdceff (1819) had pointed out the analogy of beryllium and magnesium sulphates, and Mendeléeff placed beryllium in Group II before magnesium, assuming it to be bivalent and its oxide BeO. Its atomic weight should then be 4.5 \times 2 = 9.0 and there is a vacant place between Li = 7 (univalent) and B = 11 (trivalent). Humpidge found that the specific heat of beryllium increases rapidly with temperature, becoming 0.6206 at 500° : this gives

Be = 9.8. Nilson and Pettersson (1884) found that the vapour density ($H = 1$) of beryllium chloride was 40, which agrees with BeCl_2 ($9 + 71 = 80$), but not with BeCl_3 ($13.65 + 106.5 = 120.15$).

The metal indium, which occurs in minerals with zinc, has an equivalent of 38. From its occurrence with zinc it was supposed to be bivalent (the oxide being InO), hence the atomic weight is $38 \times 2 = 76$. Indium then goes in Group II after zinc; but this position is occupied by strontium (87) and there is no place for an element of atomic weight 76. There is also no place between As = 75 and Se = 79, so that this atomic weight of indium is impossible. The vapour density, atomic heat, and isomorphism methods had not been used, and no guidance was available. Mendeléeff pointed out that if indium is trivalent (oxide In_2O_3), atomic weight $38 \times 3 = 114$, it would fill a vacant space in Group III between Cd = 112 and Sn = 118 in Groups II and IV. The chemical and physical properties agree with this. The densities are Cd 8.6, In 7.4, Sn 7.2; the basic properties of In_2O_3 are intermediate between CdO and SnO_2 ; the specific heat of indium was found to be 0.055, giving the atomic weight $6.3/0.055 = 114.5$; and indium forms alums.

In other cases the correction in the atomic weight amounted to a few units only, the valency remaining unaltered. Thus, gold was formerly placed before iridium, platinum, and osmium, in the old atomic weight sequence. Chemical analogies in the periodic table suggested the order Os, Ir, Pt, Au, and more exact atomic weights confirmed this.

Prediction of missing elements.—Mendeléeff in arranging the elements in the periodic table had to leave gaps so that chemical analogies should be preserved. The next element known after calcium ($\text{Ca} = 40$) was titanium ($\text{Ti} = 48$). But titanium if placed after calcium would come in the third group under aluminium, yet its properties show that it is 4-valent and belongs to Group IV under silicon:

Be	9	B	11	C	12	N	14
Mg	24	Al	27	Si	28	P	31
Ca	40	—	—	Ti	48	V	51
Zn	65	—	—	—	—	As	75

There are three vacant places and Mendeléeff predicted that they would be filled by elements still to be discovered, which he called *eka-boron*, *eka-aluminium* and *eka-silicon* (from the Sanskrit, *eka* = one), the properties of which he predicted from their positions in the table. These predictions were brilliantly verified by the discovery of the three elements scandium (Nilson, 1879), gallium (Lecoq de Boisbaudran, 1875) and germanium (Winkler, 1886).

The following table shows the predicted and observed properties in the case of germanium. It was said that these predictions could have been made without the Periodic Law, but no chemist seems to have thought of doing this.

EKA-SILICON (Es) predicted by Mendeléeff, 1871	GERMANIUM (Ge) discovered by Winkler, 1886.
Atomic weight 72.	Atomic weight 72.6.
Density 5.5.	Density 5.47.
Atomic volume 13.	Atomic volume 13.2.
Colour: dirty grey, giving a white powder of EsO_2 on calcination.	Metal greyish-white, giving a white powder of GeO_2 on calcination.
Metal will decompose steam with difficulty.	Metal does not decompose water.
Action of acids slight: that of alkalis more pronounced.	Metal not attacked by HCl ; dissolves in aqua regia; aqueous KOH no action, but molten KOH oxidises with incandescence.
Element obtained by action of sodium on EsO_2 or K_2EsF_6 .	Element obtained by reduction of GeO_2 by carbon, or of K_2GeF_6 by sodium.
Oxide EsO_2 refractory: sp. gr. 4.7; less basic than TiO_2 or SnO_2 , but more than SiO_2 .	Oxide GeO_2 refractory; sp. gr. 4.703; very feebly basic, forms germanates.
Hydroxide soluble in acids, but solutions readily hydrolyse with deposition of meta-hydroxide.	Acids do not pp. hydroxide from dilute alkaline solutions; from concentrated solutions, acids or CO_2 pp. GeO_2 or meta-hydroxide.
Chloride EsCl_4 a liquid, b. pt. below 100° , sp. gr. 1.9 at 0° .	GeCl_4 a liquid, b. pt. 86.5° , sp. gr. 1.887 at 18° .
Fluoride EsF_4 not gaseous.	$\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ a white crystalline solid.
Organo-metallic compounds, <i>e.g.</i> $\text{Es}(\text{C}_2\text{H}_5)_4$, b. pt. 160° , sp. gr. 0.96.	$\text{Ge}(\text{C}_2\text{H}_5)_4$, b. pt. 160° , sp. gr. slightly less than 1.0.

Results like these convinced chemists that the Periodic Law was important, and about 1890 (twenty years after it was announced) it came into fairly general use in teaching.

A new group (the inert gases) was added by Ramsay, and some gaps in the lowest part of the table were filled by radioactive elements. The Periodic Law showed the possibility of discovering new elements, and gave indications of their properties and with what known elements they are likely to occur. On the other hand, it limits the possible number of new elements; there can be no elements between helium ($\text{He} = 4$) and barium ($\text{Ba} = 137$), except possibly in the transitional group. In the lower part of the table, the question of possible new elements was difficult, since the rare earths disturbed the order. Apart from these, the gaps corresponding with elements 43, 75, 84, 85 and 87 have always been recognised, and these have since been filled, partly with information given by the periodic table. It is wrong to suppose that the Periodic System has been "superseded" by modern theories, since it is the basis of modern knowledge of atomic structure. What has happened is that the system has to some extent been *explained*.

Use of the periodic table.—The periodic table has several advantages over any other system of classification of the elements :

1. It classifies the elements in a very simple way, since only the atomic weights are needed to place the elements in the table.

2. It includes in itself some earlier methods of classification, such as that according to valency.

3. It allows the atomic weights to be checked, since if the wrong multiple of an equivalent had been taken, there would be no place for the element in the table.

4. An empty space in the table directs attention to an undiscovered element and also, from the position in the table, makes it possible to predict the properties of the element.

5. The periodic table is closely related to the structure of the atom and has proved of great service in this field. It is based on a fundamental law relating to the building up of atoms from their simpler components.

Difficulties in the periodic table.—The periodic table as given by Mendeléeff was not free from difficulties.

1. One of the most serious is the *inverted* positions of pairs of elements (A, K ; Cu, Ni ; Te, I ; Pa, Th).

2. It was difficult to fit in the rare earth elements.

3. The transitional elements occupy an exceptional position and attempts to include them in other groups were not successful.

4. The arrangement into groups overlooks some chemical analogies, as between boron and carbon, and copper and mercury, and also brings together elements with little real analogy, such as manganese and chlorine, and the alkali metals and copper, silver, and gold. Yet the analogy between successive elements in a period, although pointed out by Mendeléeff, was often neglected. The metals of the period : V, Cr, Mn, Fe, Co, Ni, are chemically related, and the sulphates $RSO_4 \cdot 7H_2O$ of Mn, Fe, Co, Ni, Cu, Zn, are isomorphous.

5. A remarkable difficulty was the position of hydrogen. It was sometimes omitted altogether, but it shares a whole period with helium. If placed in this period in Group I with the alkali-metals (to which it shows resemblance in electropositive character and in forming an alloy with palladium) there are gaps in the period with atomic weights between 1 and 4. Hydrogen as a univalent element could be placed in Group VII with the halogens. But although hydrogen is a non-metal, can be replaced atom for atom by halogens in organic compounds, forms salt-like hydrides such as NaH , and is a gas more difficult to liquefy than fluorine, yet the period might then contain unknown elements with atomic weights less than 1. The best situation is at the head of Group I, on account of the electropositive character.

Prout's hypothesis.—The differences between the atomic weights of successive elements in the various periods show regularities. The earliest, dating back to 1815 (long before the discovery of the periodic relationship) is **Prout's hypothesis**. According to this, the *atomic weights of the elements are whole multiples of that of hydrogen*. In 1816 Prout stated that the simplest explanation of this is the assumption that

the atoms of all elements are formed by the condensation of atoms of hydrogen, this element being the primary matter or protyle (Greek proté first, hule matter).

In 1812 Davy had suggested that the "undecomposed substances" [elements] are compounds of hydrogen "with another principle as yet unknown in the separate form," and that "the same ponderable matter in different electrical states, or in different arrangements, may constitute substances chemically different." This was strikingly confirmed by recent work on the structure of the atom.

Prout's hypothesis was disproved by accurate determinations of atomic weights by Berzelius, but it continued to have extraordinary fascination. Dumas and Stas in 1841 redetermined the atomic weight of carbon, finding it almost exactly 12 and showing that Berzelius had made an error in this case of no less than 2.5 per cent. When these two experimenters found in 1842 that the atomic weight of oxygen was almost exactly 16, interest in Prout's hypothesis revived. The atomic weight of chlorine is nearly 35.5, so that Marignac suggested that atomic weights are multiples of *half* the atomic weight of hydrogen, and Dumas proposed a *quarter*.

Marignac (1860) also suggested that small variations of composition of compounds would explain the deviations from whole numbers. This contains the germ of the modern theory of isotopes. Stas, beginning with "an almost complete confidence in the exactness of the law of Prout," was led by his researches to conclude that it "is only an illusion, a pure hypothesis definitely contradicted by experiment": it was also rejected by Mendeléeff.

Interest in Prout's hypothesis revived as a result of experiments by Crookes (1887) on the discharge of electricity through gases at very low pressure. Crookes assumed that electricity is carried in vacuum tubes by a very attenuated "fourth state of matter," which he identified with protyle. This was the beginning of the electrical theory of matter, which forms the subject of the following chapter.

Apart from hypothetical considerations, interesting regularities appear in the periodic system itself.

Rydberg (1914) observed that the first short period contains $2 = 2.1^2$ elements: the two short periods from Li to Ne, and from Na to A, contain each $2.2^2 = 8$ elements. The two long periods, from K to Kr, and Rb to Xe, contain each $2.3^2 = 18$ elements. These should, if the same regularity holds good, be followed by two very long periods containing each $2.4^2 = 32$ elements, of which the first is known but only a fragment of the second exists. Bohr (1921) wrote Rydberg's numbers as $2 = 1.2$, $8 = 2.4$, $18 = 3.6$, and $32 = 4.8$. Experiments on the scattering of X-rays by gases, and modern atomic theory, indicate consecutive positions for hydrogen and helium. Rydberg considered that two hypothetical gases should come between H and He, and he identified them with coronium and nebulium, evidence of which was supposed to have been found in the spectra of the sun and nebulae. The existence of coronium (supposed by Nicholson to have

an atomic weight 2.1) had been inferred from the bright green line in the spectrum of the sun during the eclipse of 1869; although traces were said by Nasini, Anderlini, and Salvadori (1893) to exist in volcanic gases, its presence on the earth is doubtful. Coronium was reported in the spectrum of the nebula of Orion by Bourget, Fabry, and Buisson (1914). In the solar eclipse of 1915 the green line was hardly visible, but a new red line was very prominent. Modern spectroscopy has shown that the peculiar lines are really due to common elements such as oxygen. Mendeléeff regarded the ether as an inactive element of atomic weight about 10^{-6} , but the existence of the ether is no longer assumed in physical theories. Modern theories of atomic structure exclude the existence of atoms lighter than those of hydrogen, or with weights between those of hydrogen and helium.

CHAPTER XXIII

ISOTOPES, CRYSTAL STRUCTURE, RADIOACTIVITY

The modern atomic theory.—The remarkable nature of the Periodic Law gave rise to many fundamental questions, some of which have received solutions in recent years, when the structure of the atom has been revealed in ever-increasing detail. Among the problems which present themselves are (1) the reason for the approximately whole-number atomic weights of some elements; (2) the explanation of the reversal of the order of atomic weights in the cases A, K; Te, I; Co, Ni; Pa, Th; (3) the reason for the occurrence of long and short periods and transitional elements, and the position of the rare earths; (4) what property of the atom determines the position of an element in the Periodic Table, since the order of the atomic weights is sometimes disturbed; (5) whether all the atoms are composed of simpler parts, and if so of how many; and (6) whether the atoms of one element can be converted into atoms of another element.

The results of the experimental investigation of these problems constitute the modern atomic theory. Although the fundamental researches in this field go back in some cases for many years, it is only since about 1910 that much progress has been made and many important results have been obtained still later.

Cathode rays.—Although the most familiar production of electrons is their emission from the hot filament of the wireless valve, the recognition of a fundamental particle of electricity was the result of experiments on the discharge of electricity in gases at low pressures, first carefully studied by Faraday.

At a low pressure (0.01 mm.) an electrical discharge in an exhausted tube proceeds as a blue glow from the cathode, normal to the cathode and independent of the position of the anode, producing a green fluorescence where it strikes the glass (Fig. 214). These cathode rays were discovered by Plücker in 1859; they are deflected by a magnet, showing that they are electrically charged. Perrin in 1895 showed directly that they are negatively electrified by collecting them in a Faraday cylinder in the tube. Sir J. J. Thomson (1897), by measuring the deflection produced by magnetic and by electric fields, found the ratio of the charge to the mass of the particles, $e/m = 1.2 \times 10^8$ coulomb

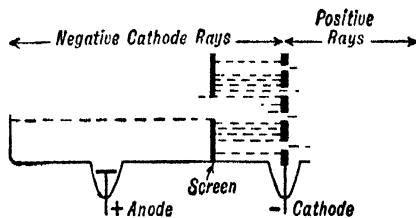


FIG. 214.—Cathode and positive rays.

they are negatively electrified by collecting them in a Faraday cylinder in the tube. Sir J. J. Thomson (1897), by measuring the deflection produced by magnetic and by electric fields, found the ratio of the charge to the mass of the particles, $e/m = 1.2 \times 10^8$ coulomb

per gm.; recent determinations give 1.772×10^8 cmb. per gm. The ratio for the hydrogen ion in electrolysis is $F/1.008 = 96.494 \times 10^3/1.008 = 9.57 \times 10^4$ (the charge being positive); the value for cathode rays is 1850 times this. There are two possibilities: (i) the charges are the same but the mass of the cathode ray particle is $1/1850$ that of the hydrogen atom; (ii) the masses are the same but the charge on the cathode ray particle is 1850 that on the hydrogen ion. Experiment decided in favour of the first. The cathode rays are free **negative electrons**. They have the same value of e/m no matter what is the material of the electrodes or the gas in the tube, and they are emitted from heated metals, by the action of ultra-violet light on metals, and in some chemical reactions. The evidence points to electrons being a *common constituent of all atoms*.

Isotopes.—If the cathode in the tube is perforated, luminous rays pass backwards through it (Goldstein, 1886), and their deflections in magnetic and electric fields show that they contain particles of atomic size, of mass m and positive charge e . These **positive rays** were investigated by Wien, Sir J. J. Thomson, and F. W. Aston.

By deflecting positive rays by means of applied electric and magnetic fields, Thomson (1913) showed that neon contains two kinds of atoms, with masses 20 and 22. Such varieties of an element were called **isotopes**. An early form of apparatus devised by Aston is shown in Fig. 215. The positive

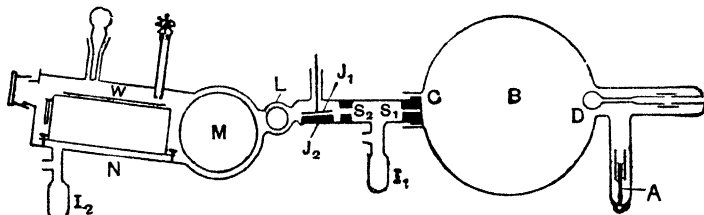


FIG. 215. Aston's positive ray apparatus.

rays produced from gas at low pressure in the bulb *B* pass through the perforated cathode *C* (the anode is *A*) and through slits $S_1 S_2$, then through the electric field of a plate condenser $J_1 J_2$, by which they are deflected downwards, and a fairly narrow pencil passes through a diaphragm (not shown) near the stopcock *L*. The rays then pass through a magnetic field at right angles to the electric field and to the plane of the paper at *M* (a section of a magnet pole), so arranged that the downward deflection due to the electric field is overcome, and they are brought to a focus on a photographic plate *W* in the camera *N*, producing a line when the plate is developed. A low pressure is maintained in the part of the apparatus to the left of the bulb *B* by means of pumps and the charcoal bulbs I_1 and I_2 , cooled in liquid air. The discharge tube *B* is about 20 cm. diameter, the anode *A* is of aluminium, as are also the cathode *C* and the metal slits S_1 and S_2 . *D* is a silica bulb which protects the opposite end of the glass bulb from being melted by the very concentrated beam of cathode rays emitted by *C*.

The particles are spread according to the values of the ratio of mass to charge m/e into a "mass spectrum," the foci of which are received on the

plate, and since a narrow ribbon of rays was defined by the slits S_1S_2 , these foci will be lines, each corresponding with a certain definite value of m/e . Some elements give lines indicating that they are mixtures of isotopes. Chlorine gives no line corresponding with the atomic weight 35.46, but two lines indicating particles of masses 35 and 37, represented as ^{35}Cl and ^{37}Cl (Fig. 216). In some cases the method described cannot be used, e.g. with metals or substances of small vapour pressure. Aston then used a method due to Gebrcke and Reichenheim, in which the anode consists of a heated strip of platinum foil with a depression containing some of the salt of the metal, and placed opposite the cathode. By applying a high positive potential to the anode, positively charged metal atoms are given off as anode rays, which can be deflected in electric and magnetic fields as before.



Aston's "Mass-Spectra and Isotopes" (Arnold)

FIG. 216. —Mass-spectra (Aston, 1921).

The lines additional to those of the isotopes of the elements indicated are due to impurities in the discharge tube.

In another method used by Dempster (1918), positive ions emitted by heated metal salts in a high vacuum pass through a potential difference, when they acquire equal energies. After passing through a slit, the ions are bent by a magnetic field into a semicircle, so that they are just able to pass through a second slit into an electroscope. With a constant magnetic field, the potential difference required to cause the ions to pass through the fixed second slit is inversely proportional to m/e for the ion, the value of which is so determined.

A more sensitive method for the detection of isotopes is the use of band spectra (p. 439). The separation of the lines in a band depends on the mass of the molecule, and in some cases instead of a regular separation expected from one kind of molecule only, there are two (or more) sets of lines in the bands, due to isotopic molecules. The hydrogen chloride spectrum shows lines corresponding to H^{35}Cl and H^{37}Cl . In this way the oxygen isotopes of masses 16, 17 and 18 were detected in the atmosphere, and also isotopes of carbon and nitrogen.

The proportion of isotopes in an isotopic mixture is very variable. In

hydrogen the atomic ratio is $^1\text{H} : ^2\text{H} = 6900 : 1$; bromine is a mixture of approximately equal parts of ^{79}Br and ^{81}Br . Apart from the isotopes of lead produced in the radioactive changes of uranium (^{206}Pb) and thorium (^{208}Pb), slight differences in atomic weights of different specimens of natural elements have been found, e.g. in atmospheric oxygen and oxygen from water in which the oxygen isotope ratio $^{16}\text{O} : ^{18}\text{O}$ is somewhat different, also with isotopes of carbon ^{12}C and ^{13}C , of boron ^{10}B and ^{11}B , and of sulphur ^{32}S and ^{34}S . The variations are sometimes quite appreciable, and the isotopic composition of an element can be determined quantitatively by means of the mass spectrograph.

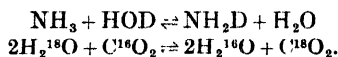
Separation of isotopes.—Isotopes can be separated in various ways; neon by *fractional diffusion*; mercury, zinc, potassium and chlorine (as hydrochloric acid) by *distillation at very low pressure*; the lithium isotopes ^6Li and ^7Li , the potassium isotopes ^{39}K , ^{40}K and ^{41}K , and the uranium isotopes ^{235}U and ^{238}U , by the *mass-spectrograph*; neon, hydrogen, water, ammonia, carbon tetrachloride and oxygen by *fractional distillation*.

If x_0 and y_0 are the volumes of two constituents in the original mixture, and x and y the volumes in the residue after diffusion, the enrichment coefficient $r = (y/y_0) \cdot (x_0/x)$ is related to the isotopic masses m_1 and m_2 by the equation $r = a \sqrt{V_0/V}$, where $a = (m_1 + m_2)/(m_1 - m_2)$; $V_0 = x_0 + y_0$; $V = x + y$. The value of a for HD and H_2 is 5, for neon 21, and for $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}$, 33. The diffusion method has been used with batteries of porous clay tubes in series, also diffusion into mercury vapour of the pumps circulating the gas. By the first method pure ^{20}Ne was obtained, and in 8 hours 1 c.c. of pure D_2 from a mixture with H_2 containing only 1 in 1000 of D_2 . A partial separation of the carbon isotopes ^{12}C and ^{13}C has been achieved by diffusion of methane. Diffusion of hydrogen and deuterium through heated palladium has also been used.

The *thermal diffusion* method has been much used. In a vertical tube containing a gas, with an axial wire heated electrically to 500° or more, the heavier molecules accumulate in the cooler region. The gas rises to the top, flows down the cold wall of the tube, and again rises in the central part. This "thermal siphoning" combines with the thermal diffusion from the hot wire, and as a result the heavier molecules accumulate at the bottom of the tube and the lighter molecules at the top. A very effective separation can be obtained.

The electrolytic method is most successful in the separation of hydrogen and deuterium from water (p. 176). A slight separation of oxygen isotopes is also effected.

Some separation of isotopes has been achieved by chemical means, generally by exchange reactions of the type



In a photochemical method phosgene (COCl_2 , containing the chlorine isotopes 35 and 37, is exposed to light, when molecules containing ^{36}Cl are preferentially decomposed (in presence of a trace of iodine). The chlorine is absorbed by mercury and has an atomic weight lower than normal.

TABLE OF ISOTOPES

The isotopic masses A rounded off to whole numbers of natural elements of atomic number $Z = 0$ (the neutron : see p. 409) to 92 are given. The order is that of masses, not of abundance of occurrence. Radioactive species are starred.

Z		A	Z		A
0	n	1	48	Cd	106, 108, 110, 111, 112, 113, 114, 116
1	H	1, 2	49	In	113, 115
2	He	3, 4	50	Sn	112, 114, 115, 116, 117, 118, 119, 120, 122, 124
3	Li	6, 7	51	Sb	121, 123
4	Be	9	52	Te	120, 122, 123, 124, 125, 126, 128, 130
5	B	10, 11	53	I	127
6	C	12, 13	54	Xe	124, 126, 128, 129, 130, 131, 132, 134, 136
7	N	14, 15	55	Cs	133
8	O	16, 17, 18	56	Ba	130, 132, 134, 135, 136, 137, 138
9	F	19	57	La	139
10	Ne	20, 21, 22	58	Ce	136, 138, 140, 142
11	Na	23	59	Pr	141
12	Mg	24, 25, 26	60	Nd	142, 143, 144, 145, 146, 148, 150
13	Al	27	62	Sm	144, 147, *148, 149, 150, 152, 154
14	Si	28, 29, 30	63	Eu	151, 153
15	P	31	64	Gd	152, 154, 155, 156, 157, 158, 160
16	S	32, 33, 34, 36	65	Tb	159
17	Cl	35, 37	66	Dy	158, 160, 161, 162, 163, 164
18	A	36, 38, 40	67	Ho	165
19	K	39, *40, 41	68	Er	162, 164, 166, 167, 168, 170
20	Ca	40, 42, 43, 44, 46, 48	69	Tm	169
21	Sc	45	70	Yb	168, 170, 171, 172, 173, 174, 176
22	Ti	46, 47, 48, 49, 50	71	Lu	175, *176
23	V	51	72	Hf	172?, 174, 176, 177, 178, 179, 180
24	Cr	50, 52, 53, 54	73	Ta	181
25	Mn	55	74	W	180, 182, 183, 184, 186
26	Fe	54, 56, 57, 58	75	Re	185, *187
27	Co	59	76	Os	184, 186, 187, 188, 189, 190, 192
28	Ni	58, 60, 61, 62, 64	77	Ir	191, 193
29*	Cu	63, 65	78	Pt	192, 194, 195, 196, 198
30	Zn	64, 66, 67, 68, 70	79	Au	197
31	Ga	69, 71	80	Hg	196, 198, 199, 200, 201, 202, 204
32	Ge	70, 72, 73, 74, 76	81	Tl	203, 205
33	As	75	82	Pb	204, 206, 207, 208
34	Se	74, 76, 77, 78, 80, 82	83	Bi	209
35	Br	79, 81	90	Th	*232
36	Kr	78, 80, 82, 83, 84, 86	91	Pa	*231
37	Rb	85, *87	92	U	*234, *235, *238
38	Sr	84, 86, 87, 88			
39	Y	89			
40	Zr	90, 91, 92, 94, 96			
41	Nb	93			
42	Mo	92, 94, 95, 96, 97, 98, 100			
44	Ru	96, 98, 99, 100, 101, 102, 104			
45	Rh	103			
46	Pd	102, 104, 105, 106, 108, 110			
47	Ag	107, 109			

Several isotopes of different elements have the same mass (*isobars*), e.g. A, K 40; Ni, Zn 64; Kr, Sr 86. Elements of odd atomic number are either simple or (except K) have only two isotopes, elements of even atomic number have many isotopes. The isotopes of elements of odd atomic number have odd masses usually differing by two units. The atomic masses

of isotopes are referred to the oxygen isotope of mass 16, viz. $^{16}\text{O} = 16$, and actually differ slightly from whole numbers, in the case of hydrogen ($^1\text{H} = 1.0081$, $^2\text{H} = \text{D} = 2.0147$) appreciably.

Packing fraction.--The difference between the isotopic mass and the nearest whole number, divided by the isotopic mass, is called the packing fraction. Thus, the mass of ^{58}Ni is 57.942, hence the packing fraction is $-0.058/58 = -0.001$. Packing fractions are either positive or negative, according as the atomic masses on the basis $^{16}\text{O} = 16$ are larger or smaller, respectively, than the nearest whole number. Negative values appear with

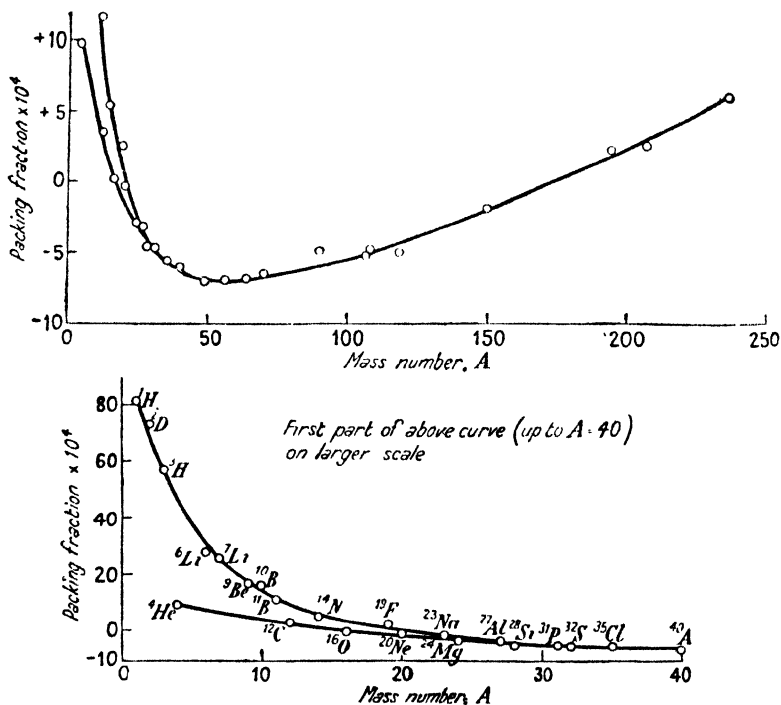


FIG. 217.

mass number 20 (neon), and the curve of packing fractions plotted against mass number A has a minimum at $A = 50$, afterwards rising to a positive value at $A = 25$. Below $A = 25$ the curve has two branches (Fig. 217), the lower branch corresponding with elements for which $A = 4 \times$ mass of ^4He .

Calculation of atomic weights. The atomic weight of a natural element is an average value of the atomic masses of the isotopes it contains. The ratios of the proportions of the isotopes in the natural element are called the **abundance ratios**. The atomic weight of the natural element may be calculated from the exact masses of the isotopes, obtained by correcting the whole-number values by the packing fractions taken from the curve of Fig. 217, and from the abundance ratios of these. For example, the abundance ratio of the europium isotopes in the natural element is $^{151}\text{Eu}/^{153}\text{Eu} = 0.963$,

hence the atomic weight referred to $^{16}\text{O} = 16$, uncorrected for the deviations of the isotopic masses from whole numbers, is $152.019 \cdot 0.037 + 151 + 0.963 \times 153$. The packing fraction for $A = 152$ is -0.0002 , hence the mass defect is $(-0.0002) \cdot 152 = -0.030$. The exact atomic mass ($^{16}\text{O} = 16$) is $152.019 - 0.030 = 151.989$, and since the atomic masses referred to $^{16}\text{O} = 16$ are converted to the ordinary or chemical atomic weights, on the basis of ordinary oxygen, $\text{O} = 16$ (the isotopic mixture), by division by 1.000275 , the chemical atomic weight of europium is $151.989/1.000275 = 151.95$.

X-rays.—When cathode rays strike a material target in the X-ray tube, consisting of a metal plate called an *anti-cathode*, this emits a penetrating radiation which passes outside the tube, and can pass freely through paper, wood, aluminium, and flesh, but is largely absorbed by lead, platinum, glass, or bone. These X-rays (Röntgen, 1895) may be so penetrating as to pass through two inches of steel. They affect a photographic plate, cause fluorescence of barium platinocyanide etc., and render a gas conducting or produce ionisation in it, charged particles being formed. A gold-leaf electroscope rapidly loses its charge when exposed to X-rays, since the surrounding air conducts away the charge. The X-rays consist of **electromagnetic waves** similar to light but of much smaller wave-length. The wave-length λ depends partly on the composition of the anti-cathode or "target," and partly on the applied voltage.

X-rays and crystals.—For a long time it was not possible to diffract X-rays by matter, since the wave-lengths are much smaller than those of light. Friedrich, Knipping, and Laue (1912) showed that X-rays are diffracted in passing through crystals, and further work of W. H. and W. L. Bragg showed that they are reflected from crystal surfaces at definite angles of incidence in the same way as light from a diffraction grating.

If the primary X-rays are homogenous (*i.e.* all of the same wave-length) the series of directions along which reflexions occur are obtained by giving the values 1, 2, 3, . . . to n in the general equation $2d \sin \theta = n\lambda$, where λ is the wave-length. In the ordinary diffraction grating, d is the space between the rulings; in the case of X-ray reflexion from crystals, d is identified with the distance between planes in the crystal corresponding with the densest arrangement of the atoms.

In Fig. 218 a parallel beam of X-rays of wave-length λ is shown reflected from various planes of atoms distant d apart, θ being the angle of incidence with the crystal surface. The difference of path for two rays is:

$$\begin{aligned} CD + DB - AB &= DB - DE \\ &= DF - DE = EF = 2d \sin \theta. \end{aligned}$$

The two rays are in phase and reinforce each other when this is a whole multiple n of the wave-length λ , or $2d \sin \theta = n\lambda$. If d is known λ can be found, and conversely.

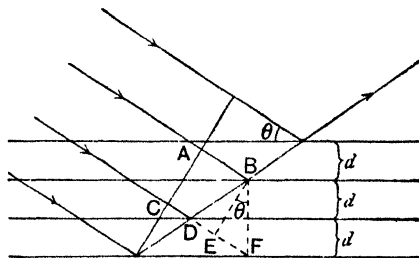


FIG. 218. — Reflexion of X-rays from a crystal.

The original apparatus used by the Braggs is shown in Fig. 219. The rays from the anti-cathode of the X-ray bulb are constricted to a narrow pencil by the lead slits, *A* and *B*,

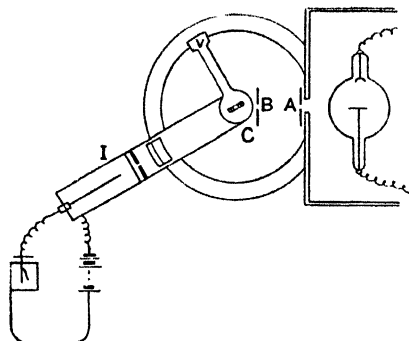


FIG. 219.—X-ray spectrometer.

and impinge on the crystal *C*, moving over a graduated circle. The reflected beams are received in an ionisation chamber *I*, also pivoted at the centre of the X-ray spectrometer, and render the gas contained in the chamber, usually sulphur dioxide, a conductor of electricity. The intensity of the current passing through the gas, measured by an electroscopes, indicates the positions of reflexion from the crystal. The ionisation occurs with homogeneous X-rays at angles corresponding with the different orders of spectra given by the equation $2d \sin \theta = n\lambda$. In the graph of the current against the angle of incidence, peaks occur corresponding to definite wave-lengths in the X-rays, and these are repeated as the spectra of different orders are passed over. In the case of a platinum anti-cathode, for example, three peaks are found, showing that the X-radiation of platinum is a mixture of three characteristic wave-lengths. These reappear whatever the nature of the crystal used for reflexion.

This apparatus has been modified and improved, the detection of the X-ray beams being photographic.

The original method of Laue, viz., the production of a diffraction pattern of spots by a beam of rays passing through a plate of crystal cut in a particular direction, is also used in crystal analysis.

A third method was developed by Debye and Scherrer and by Hull, and is called the *powder method*. A beam of X-rays is intensely reflected from the structural layers in a crystal only when it meets them at proper angles. A powder consists of innumerable small crystals orientated in chaotic fashion, but there will always be a number in correct orientation for reflexion of a beam of homogeneous X-rays transmitted through the powder. The powder is contained in a very thin glass tube (shown on the axis of the cylinder in Fig. 220) parallel to the slit or in the direction of a beam transmitted through a small hole, or else the powder is spread over a plate arranged for reflexion as in Bragg's apparatus. When the transmission method is used the pencil of rays is spread into a series of cones, the intersections of which on the cylindrical photographic film produce a series of segments of circles arranged on each side of the central spot corresponding with the axial undeviated pencil (Fig. 220).

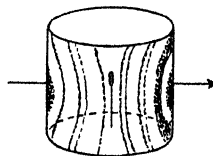


FIG. 220.—The powder method of X-ray analysis.

Crystal lattices.—By making use of the principle that the intensity of the radiation scattered from an atom is proportional to the number of electrons in the atom (and thus according to the modern theory of atomic structure p. 404, to the atomic number of the atom) it could be shown that the two strong reflexions from potassium chloride were due to the atoms K and Cl, of approximately equal weight. In this way the crystal structure shown in Fig. 221 was found, the *centres* of the potassium atoms being represented by circles and those of the chlorine atoms by dots. The particles are not the molecules KCl but the atoms (or ions) K and Cl arranged in a cubic lattice.

The existence of separate ions in crystals such as rock-salt is made probable by: (1) the intensities of X-ray reflexions (Debye and Scherrer, Li^+ and F^- in LiF ; Gerlach and Pauli, Mg^{++} and O^{--} in MgO); (2) the reflexion of infra-red rays (*residual rays*); (3) the ionisation in solution and in the fused state.

If in Fig. 221 we consider the atoms \circ as sodium and \bullet as chlorine, and the side of the cube as a , then $d = a/2$. There are 14 chlorine atoms, eight of which at the corners belong each to eight cubical lattices which may be packed around it, only one of these being shown. The other six are on the faces, and each is common to two cubical lattices, one of which is shown. Hence, of the 14 atoms a single cubical lattice has a share of eight $\frac{1}{8}$ atoms, and six $\frac{1}{2}$ atoms, or $1 + 3 = 4$ atoms in all. Of the 13 sodium atoms shown, one is at the centre and 12 are in positions where each is shared by four lattices (one only shown), *i.e.* in one lattice there are $1 + 3 = 4$ atoms. The volume of the lattice is $a^3 = 8d^3$, where a is the side of the lattice and $d = \frac{1}{2}a$ is the distance between the planes of atoms. Thus d^3 is associated with the mass of one-eighth of 4 sodium atoms and 4 chlorine atoms, or half a molecule of NaCl. This is $\frac{1}{2}M/N = \frac{1}{2} \times 58.5/6.03 \times 10^{23}$ gm., where M = molecular weight, N = Avogadro's number. But this mass is also equal to d^3 multiplied by the density of rock-salt, 2.17, hence $\frac{1}{2} \times 58.5/6.03 \times 10^{23} = 2.17 \times d^3$, or $d = 2.82 \times 10^{-8}$ cm.

By means of this value, the wave-length of any kind of homogeneous X-rays may be found by using rock-salt as the reflecting crystal and using the equation $2d \sin \theta = n\lambda$.

This calculation can be reversed, and if the distance d is calculated from the wave-lengths of the X-rays used, and the density of the crystal is accurately determined, the molecular weight M may be calculated. If the atomic weights of all the elements but one composing the crystal are known, the unknown atomic weight may be calculated from the molecular weight of the crystal. The density of the solid may also be found by another modification of the calculation.

Cubic lattices.—Before the use of X-ray analysis, crystallographers had arrived at the conviction that the particles in a crystal are arranged at the points of different types of lattice structures (p. 357), and even

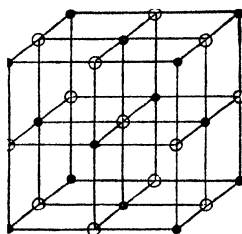


FIG. 221.—Arrangement of atoms in potassium or sodium chloride lattice.

that the particles are often atoms, not molecules. The analysis of crystals by X-rays has confirmed this.

The simplest lattice is the cubic, of which there are three types, viz. the **simple cubic lattice**, the **body-centred cubic lattice**, and the **face-centred cubic lattice**. The simple cubic lattice is shown as one of the eight units in Fig. 221, the body-centred cubic lattice as *A* in Fig. 222, and the face-centred cubic lattice as one of the eight units in *B* in Fig. 222. In the first the unit cell has eight atoms at its corners, in the second there is in addition one atom at the centre of the cube, and in the third there are six atoms at the centres of the faces of the simple cubic lattice. The body-centred cubic lattice may be produced by the interpenetration of two simple cubic lattices so that the corners of one lattice occupy the centres of the cubes of the second, as shown in *C* Fig. 222. In each unit cell of the body-centred lattice there are $1 + 8/8 = 2$ atoms, whilst the unit cell of the simple cubic lattice contains $8/8 = 1$ atom. The

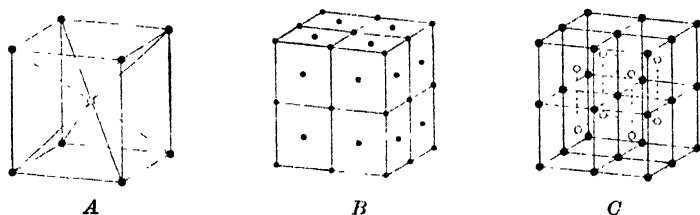


FIG. 222.—Body-centred and face-centred cubic lattices.

unit cell of the face-centred lattice shares $1/8$ of each corner atom and $1/2$ of the atom at the centre of each of the six faces, and thus contains $8/8 + 6/2 = 4$ atoms.

The following metals crystallise in *face-centred* cubic lattices: Al, Ca, γ -Fe, β -Co, α -Ni, Cu, Rh, Pd, Ag, β -Cu, Ir, Pt, Au, Pb, Th, Sr; the non-metal argon also crystallises in this system. In *body-centred* cubic lattices crystallise: Li, Na, K, Rb, Cs, V, Nb, Ta, Cr, Mo, W, α -Mn, α -Fe. (The different allotropic forms are designated α , β , etc.)

CsCl crystallises in a lattice in which each Cs atom is surrounded by 8 Cl atoms Fig. 222 *A*, but since each of the latter is shared by 8 unit cubes, the unit cell contains 1 Cs atom + $8/8$ or 1 Cl atom, or one CsCl molecule.

The lattice of potassium, sodium and rubidium halides, is the simple cubic (Fig. 221), with atoms of alkali metal and halogen alternately occupying the lattice points. Each small cube contains $4 \times \frac{1}{8} = \frac{1}{2}$ an atom of each element. Each halogen atom is surrounded by six equidistant metal atoms, and *vice versa*. (The metal and halogen atoms are really the *ions*, e.g. Na^+ and Cl^-). The rock-salt lattice may be produced by the interpenetration of two face-centred cubic lattices, one of metal ions and one of halogen ions. Each crystallographic elementary cube (the whole figure) contains eight cubelets, and hence 4 atoms each of metal ion and halogen ion.

It is noteworthy that the simple cubic lattice structure (Fig. 221) is not represented among metal crystals.

Hexagonal lattices.—The arrangement of atoms in the face-centred cubic lattice is the *closest packing of spheres*. In a layer of equal spheres in contact there are triangular spaces between every three, and in each triangular space another sphere may be placed to form a second layer. In Fig. 223 *a* the centres of the lower spheres are shown as ● and those in the second row as ○. A third layer of spheres may be put on in two ways. Either they may be placed in the positions shown by ⊙, when the face-centred cubic lattice is obtained, built up on the octahedral surface (Fig. 223 *b*); or they may be arranged in the positions shown by ●, *i.e.* vertically above the atoms in the first layer, when a lattice with hexagonal symmetry is obtained, *viz.* the *hexagonal closest packing of spheres*: it consists of two interpenetrating hexagonal lattices, the first comprising the atoms in the layers 1, 3, 5, ... , and the second the atoms in the layers 2, 4, 6, The ratio of the axes (p. 353) is $c : a = 1.633 : 1$ for equal spheres.

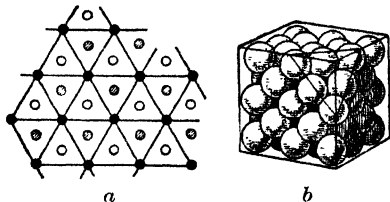


FIG. 223.—Close packing of spheres to form face-centred cubic and closest-packed hexagonal lattices.

In *hexagonal* lattices crystallise Be, Mg, Zn, Cd, α -Ce, Ti, Zr, Hf, α -Co, Ru, and Os. The distances between the atoms in all these lattices vary from about 2.5 to 4.5 A.U.

Metals crystallising in *tetragonal* lattices are germanium and white tin; in the *trigonal* lattice (which may be regarded as an elongated cube) crystallise arsenic, antimony and bismuth.

Some important lattice types.—The *diamond* lattice may be constructed by taking a face-centred cubic lattice of carbon atoms and putting a carbon atom in the centre of *alternate* cubelets as shown in Fig. 224 (*a*). Each carbon atom forms the centre of a regular tetrahedron, the corners of which are occupied by four carbon atoms, as may be seen by drawing the lattice as in Fig. 224 (*b*).

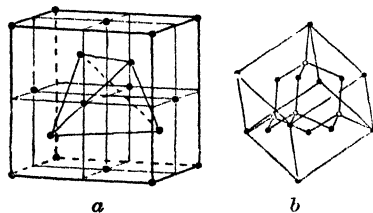


FIG. 224.—The diamond lattice.

Diamond is an example of an *atomic* lattice in which the atoms are linked by directed valency forces, as contrasted with the *ionic* lattice of an alkali halide such as sodium chloride, in which the separate charged ions are not linked by directed valencies but exert undirected electrostatic forces on one another. Silicon and grey tin crystallise in diamond lattices.

The *zinc blende* lattice is similar to that of diamond: each zinc atom is at the centre of a tetrahedron of sulphur atoms and each sulphur atom at the centre of a tetrahedron of zinc atoms. The *wurtzite* lattice (the second form of zinc sulphide) is formed from the zinc blende lattice by rotating alternate planes about an angle of 60° around the vertical

axis. The tetrahedral symmetry is not disturbed but the arrangement (Fig. 225) is different from that in diamond.

The fluorspar lattice is made up of a face-centred lattice of calcium ions penetrated by a simple cubic lattice of fluorine ions, so that the corners of this lie on the quarter lengths of the diagonals joining the

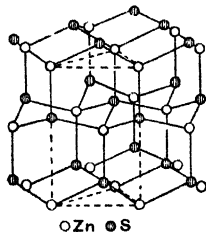


Fig. 225.—Wurtzite lattice.

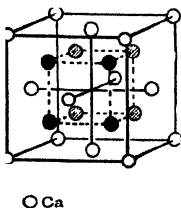


Fig. 226.—Fluorspar lattice.

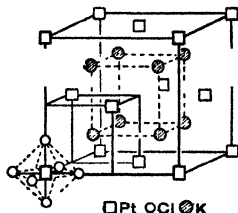


Fig. 227.—Lattice of K_2PtCl_6 .

calcium ions (Fig. 226). Each Ca^{++} ion is surrounded by $8F^-$ ions, each F^- ion by $4Ca^{++}$ ions. In the elementary cube are $8/8 + 6/2 = 4Ca^{++}$ ions and $8F^-$ ions (corresponding with the formula CaF_2). The F^- ions lie on the corners of a half-sized inner cube, as shown.

An interesting cubic lattice is that of K_2PtCl_6 (Fig. 227). This may be regarded as a fluorspar lattice in which F^- is replaced by K^+ , and each Ca^{++} by $PtCl_6^{--}$. In the complex ion $PtCl_6^{--}$, the central Pt atom is surrounded by six Cl^- ions in octahedral arrangement, thus confirming the assumption of Werner. (For simplicity only one $PtCl_6^{--}$ is shown in full.)

As a more complicated example we may consider the calcite lattice (Fig. 228). This may be regarded (not quite strictly) as a deformed rock-salt lattice. The latter is imagined stood on a diagonal (looked at from above in the figure), all the Na^+ ions replaced by Ca^{++} ions and all Cl^- ions by carbon atoms, each surrounded by a triangle of 3 oxygen atoms in a plane at right angles to the diagonal (the plane of the paper); then on account of the space occupied by these oxygens the cube expands in a horizontal direction and gives the cleavage rhombohedron of calcspar. Calcium and carbon atoms are spaced at equal intervals along the axis of the crystal, and each carbon is surrounded by three oxygens, forming the carbonate ion CO_3^{--} .

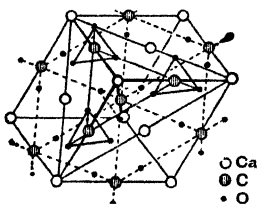


Fig. 228.—Calcite lattice.

The graphite lattice consists of flat hexagonal rings of carbon atoms arranged in equidistant layers, such that the atoms in alternate layers are in similar positions in the hexagons (Fig. 229). In these planes, which correspond with the cleavage planes, each carbon atom is surrounded by *three* other equidistant atoms; the fourth valency is directed towards an atom alternately above and below the plane and

at a much greater distance, and is hence very much weaker, as appears in the ready cleavage of graphite in the direction of the planes of hexagons.

Besides the above lattice types, there are others, some described elsewhere, e.g. the *perovskite lattice* (p. 767) The *tetragonal lattice* may be regarded as an elongated cube with eight particles at the corners. The *calcium carbide lattice* resembles a rock-salt lattice in which alternate points are occupied by Ca^{++} and rod-shaped $[\text{C}\equiv\text{C}]^{--}$ ions with their axes parallel to the cube edges, whilst in the *pyrites lattice* (p. 934) the $-\text{S}-\text{S}-$ groups are inclined.

Experiment suggests that actual crystals are not perfect lattices but consist of aggregates of innumerable tiny "blocks," each part of a perfect lattice, joined together by loose ions which alone take part in the conduction of heat and electricity. Between these aggregates are, therefore, "cracks," similar to the layers of mortar between the bricks in a house, and the irregularly arranged ions in the cracks are those which cement the blocks together and act as conductors (Snekal, 1927). Each lattice block may contain about 10,000 ions or molecules.

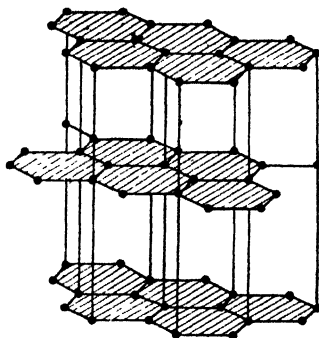


FIG. 229.—Linking of carbon atoms in graphite.

Atomic numbers.—Barkla, and Kaye (1909), found that a solid element when bombarded by a sufficiently rapid stream of cathode rays emits a characteristic X-radiation. This may be resolved into a spectrum by reflexion from a crystal, as explained on p. 387. Moseley (1913-14) used a crystal of potassium ferrocyanide and photographed the spectra of various elements.

The elements (e.g., W, Fe, Cu) or their solid compounds (e.g. KCl) were used as anticathodes in an X-ray bulb, mounted on a trolley inside the bulb so that they could be brought in succession in front of the cathode. Several kinds of rays, the *K*, *L*, *M*, *N* and *O*, have been detected, the first two by Moseley and the others by later workers. The *K*-radiations are of the shortest wave-length and are emitted by all elements. The *L*-radiation, shown from copper and elements of higher atomic weight, is of longer wave-length than the *K*-radiation, and the *M*, *N*, and *O*-radiations, shown by heavier elements, are of still longer wave-length. The *K*-radiation of each element consists of four lines, but these appear as two pairs in each of which the two lines are very close together and were not resolved in Moseley's photographs. The *L*-radiation gives a larger number of lines than the *K*; in the case of tungsten, Siegbahn measured eighteen lines in the *L* spectrum.

The *K* spectra obtained by Moseley consisted in all cases of two lines $K\alpha$ and $K\beta$ (really the two *K* pairs), one stronger than the other, the

wave-lengths of which decreased in a regular manner as the atomic weights increased. In Fig. 230, given by Moseley, the spectra are placed approximately in register, parts representing the same angle of reflexion by the crystal being in the same vertical line.

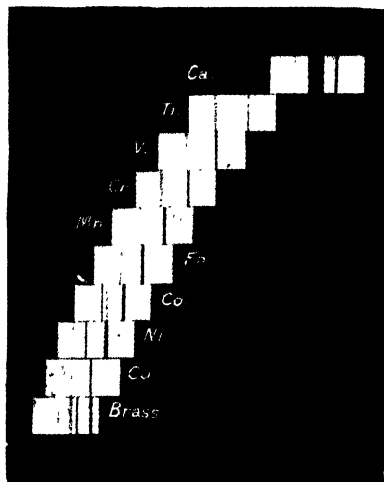


FIG. 230.—X-ray spectra (Moseley).
K-rays.

The elements, beginning with Ca at the top, are in the order of their *atomic numbers*, running from Ca 20 to Zn 30, the element Sc (No. 21) being missing. The Zn lines, with those of Cu, are shown by brass. The Co spectrum shows a faint Ni line due to impurity. The gap where Sc should come is clearly seen, since the Ca lines are shifted much more to the right in comparison with those of Ti than in any other pair in the diagram. It was found that with increasing atomic number the wave-length becomes increasingly smaller.

The frequencies ν are given by $c = n\lambda$, where c is the velocity of light. Generally, the *wave-number* $\nu \div \lambda$ is used instead of the frequency.

The square-roots of the wave-numbers of corresponding strong $K\alpha$ lines in the spectra of successive elements taken in the order of their *atomic numbers* give practically a straight line. In Fig. 231, the square-roots of the frequencies of the K , L , M , and N series are plotted against the atomic numbers. If ν is the wave-number of the $K\alpha$ line, ν_0 a constant (Rydberg's constant), and N the atomic number, then Moseley found that :

$$Q = \sqrt{\nu/\nu_0} = N - 1.$$

Element	-	-	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic weight	-	-	40	45	48	51	52	55	56	59	58.5	63	65
Q	-	-	19	-	21	22	23	24	25	26	27	28	29
N	-	-	20	21	22	23	24	25	26	27	28	29	30

Moseley's law shows that the order of values of Q is the same as that of the elements in the periodic table, although in some cases (*e.g.* Co and Ni ; Te, I) the order of atomic weights is reversed. The atomic numbers of Cl and K, deduced from the equation, are 17 and 19, leaving a gap, 18, for argon, although the latter has an atomic weight higher than that of potassium. Moseley's law gives the places in the sequence of atomic numbers where there are missing elements. In this way the elements of number 43, 61, 72, 75, 85 and 87 were found to be missing, and these were afterwards discovered.

Since all isotopes of an element occupy the same place in the Periodic Table they have the same atomic number and the same X-ray spectrum. This has been confirmed with some isotopes of lead.

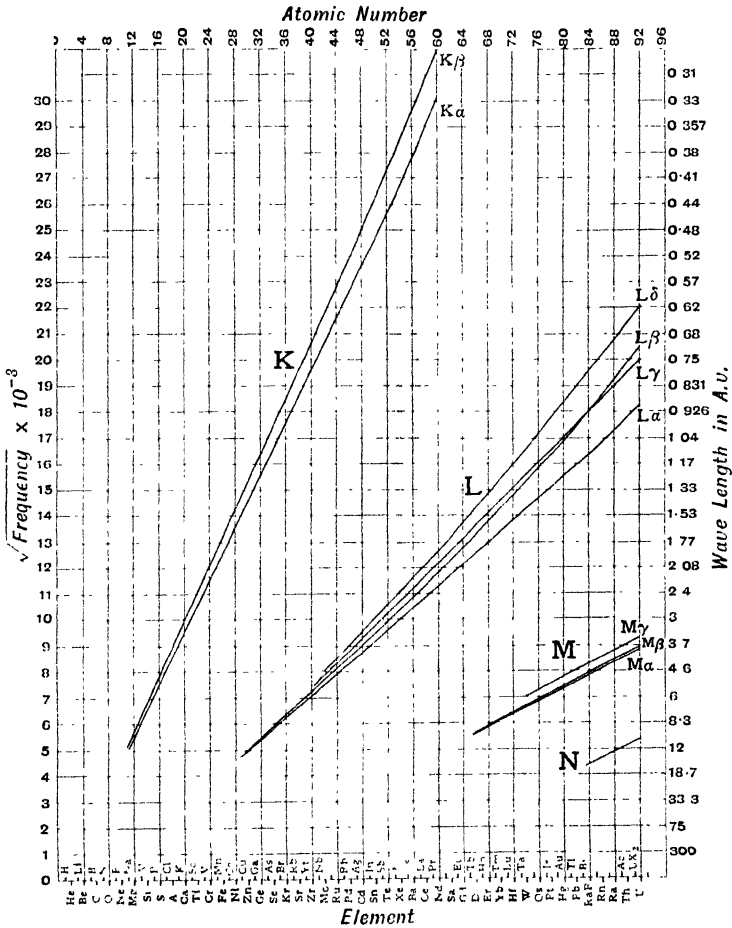


FIG. 231.

Moseley's results show that the atomic number is a property of the atom more fundamental than the atomic weight, and he suggested that this was the positive charge on the nucleus of the atom.

This suggestion, also put forward by van den Broek (1913), is the basis of Rutherford's theory of atomic structure (p. 404). According to this the very small positively charged atomic nucleus is surrounded at relatively great distances by negative electrons. Since the atom is neutral, the total number of electrons is equal to the positive nuclear charge in electron units, i.e. to the atomic number.

Refinements in X-ray spectroscopy show that the linear character of the *L*, *M*, *N* and *O* series is only approximate, and the curves show definite changes of direction (Fig. 232). The ordinates are values of $\sqrt{\nu/\nu_0}$, where ν_0 is Rydberg's constant. These breaks are important in the theory of atomic structure, since they appear at the beginning and end of successions of closely related elements, e.g. Sc to Cu; Y to Ag; etc. In these the

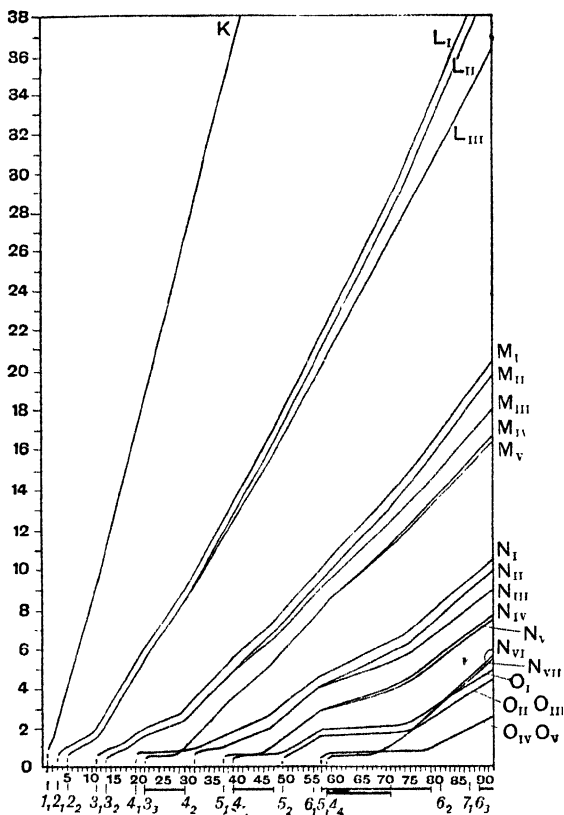


FIG. 232.

transition from one element to the next, instead of leading to a marked change of properties produces little change, and since the relation to the transitional elements of Group VIII is apparent, these sequences of elements are called "transitional series." This behaviour is very marked in the group of the rare earth elements (Nos. 57-71).

Radioactivity.—In 1896 Becquerel found that uranium salts could affect a photographic plate through a layer of black paper, and also discharge an electroscope. Thorium compounds were found by Schmidt and by Mme Curie in 1898 to have similar properties. The substances were called **radioactive**, from their property of emitting radiations of

the kind described. In the study of radioactivity the following methods are used :

- (1) The action on a photographic plate.
- (2) The phosphorescence of platinocyanides, willemite (zinc silicate), kunzite, and Sidot's blende (zinc sulphide).
- (3) The ionisation of gases.

The most convenient is the third method ; the ionisation, which makes the gas conducting, is detected and measured by the gold-leaf electroscope (Fig. 233). The strip of gold-leaf *G* is attached to the vertical rod *R*, supported by a horizontal rod *K* insulated on blocks of sulphur *S*, and terminating in a metal plate *B*. Below is a second metal plate *A*, on which the material to be tested is placed. The gold-leaf is observed through a micrometer eye-piece, the leaf being given a charge through the wire *M*, which is insulated in a sulphur stopper *S*, and can be swung away from the rod *R* when the latter is charged. If the substance *C* is radioactive, the air between *A* and *B* becomes conducting, owing to the production of positive and negative gaseous ions, and the charge leaks away at a rate which may be observed by the fall of the gold leaf. The electroscope is much the most sensitive analytical instrument known, since 10^{-12} gm. of radioactive material can be recognised.

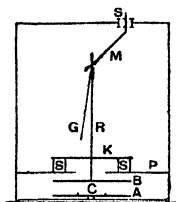


FIG. 233.—Gold-leaf electroscope.

Radium.—By means of the ionisation method Mme Curie found that the native uranium ore *pitchblende* (mostly uranium oxide U_3O_8) was more active for the same weight of uranium than a purified uranium salt, and she suspected that this was due to the presence in the ore of a new element much more radioactive than uranium. She succeeded in isolating from pitchblende an intensely active substance ; this was a salt of a new element radium. It had an activity a million times that of uranium. In highly purified specimens this activity is doubled.

The separation of the radium from pitchblende is laborious. The radium accumulates in the barium separated from the residues. Radium and barium chlorides are separated by a long series of fractional crystallisations ; with the bromides eight crystallisations suffice.

A former source of radium compounds was the *carnotite* of Colorado, with 5 to 10 mgm. of Ra per ton. Rich deposits of pitchblende in the Belgian Congo superseded carnotite, and there are rich deposits of pitchblende in the Great Bear Lake territory in N.W. Canada.

Radium compounds are isomorphous with those of barium ; the ratio of chlorine to radium in the chloride is 35.5 : 113, so that on the assumption that the formula is $RaCl_2$, the atomic weight of radium is 226. Hönigschmid from the ratio $RaCl_2 : RaBr_2$ found $Ra = 225.97$. Radium is an element of the alkaline-earth metals group in Group II. The crystals of the pure salts are colourless ; if they contain barium they are pink. The solution in water forms hydrogen peroxide and evolves oxygen and hydrogen, and the solid salts ozonise air. In the dark they

shine with a green phosphorescent glow. Radium chloride melts at a high temperature and solidifies to a glassy mass which (unlike the salt containing water) emits an intense bluish-violet light. In accordance with the behaviour of metals of its group, radium sulphate is less soluble than barium sulphate. In the bunsen flame radium compounds give a fine carmine tint, and the spectrum is analogous to those of other elements in the group. Glass is coloured violet or brown by radium rays, but the colour is discharged by heating nearly to the softening point.

Metallic radium was obtained by Mme Curie and Debierne in 1910 by electrolysing a solution of the chloride with a mercury cathode and separating the mercury from the amalgam by distillation. It is a white metal, m. pt. 960° , which rapidly tarnishes in air, forms a nitride, and decomposes water with evolution of hydrogen.

Rays from radioactive substances.—By interposing sheets of metal foil and superposing powerful magnetic fields in the electroscopie method, it was found that radium emits three kinds of rays (Fig. 234) :

1. The α -rays : positively charged particles easily absorbed by thin metal foil and having a limited range in air (7 cm. when emitted from $\text{Ra}^{(C)}$).
2. The β -rays : negatively charged particles identical with free negative electrons, emitted with speeds approaching the velocity of light and often able to penetrate thin sheets of aluminium.
3. The γ -rays : not deflected by magnetic fields, consisting of waves identical with very short X-rays (wave-length, $1.3 \cdot 10^{-7}$ to $7 \cdot 10^{-10}$ mm.), and capable of penetrating several cm. of lead.

The deflexions produced by a magnetic field are seen in Fig. 234 to be in opposite directions with the α - and β -rays : the γ -rays are undeflected.

The α -rays have a shorter range than the β -rays.

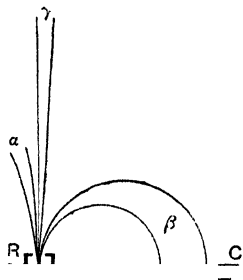


Fig. 234. Magnetic deflection of rays from radium.

The phosphorescence effects of radium are mainly due to the α -rays, which with their large mass and high velocity ($\frac{1}{15}$ to $\frac{1}{10}$ that of light), have large kinetic energies. In the spinthariscopie (p. 125) the impact of each α -particle on the screen produces a bright flash, and in this way the particles can be counted. Lord Rutherford found for the α -rays the value e/m (charge/mass) = 5.07×10^4 emb./gm., and Rutherford and Robinson 4.82×10^4 emb./gm.,

almost exactly half that for the hydrogen ion in electrolysis. They may, therefore, consist of atoms of weight 4 (helium), with two unit charges. By sealing radium emanation in a thin glass tube, Rutherford and Roysds (1908) found that α -particles escaped into an outer vacuous tube fitted with electrodes and, on passing a discharge, the helium spectrum was detected. Rutherford and Geiger measured the charge

conveyed by a counted number of α -particles and found the charge on each to be 3.1×10^{-19} emb., hence $m = 0.66 \times 10^{-23}$ gm. The mass of the hydrogen atom is 1.6×10^{-24} gm., hence the atomic weight of the α -particle is close to 4.

The α -particle is regarded as a helium atom which has lost two negative electrons. The diameter of the α -particle is very small compared with that of the helium atom. The speed of α -particles emitted by radium is about 2×10^9 cm. per sec., hence the kinetic energy is 1.36×10^{-5} erg, or 2.4×10^9 times that of a gas molecule at 0° (p. 122). This large energy accounts for the phosphorescence effects and for most of the heat evolved by radium, which amounts to 25.5 g. cal. per gm. of radium per hour. Each α -particle from RaC' ionises 237,000 gas molecules in its passage through air.

Although the β -rays are more penetrating to matter in bulk than the α -rays, on account of their smaller size and higher velocity, they are more deflected in encounters with individual atoms than are α -rays. Their paths deviate much from straight lines, as has been shown by the Wilson method (p. 403): they are frequently deflected through 180° . On account of its smaller mass and kinetic energy a β -particle produces much less ionisation for 1 cm. path than an α -particle: the total number of ions produced in air by β -rays from 1 gm. of radium in equilibrium with its products of disintegration is 9×10^{14} per sec.

The activity of radium is unaffected by temperature: it is the same in liquid air as at a red heat. In this respect, radioactive changes differ from ordinary chemical reactions, the velocity of which is largely influenced by temperature.

Radium emanation.—It was noticed that a gas, called *radium emanation*, is continually evolved from radium, which may be swept away by a current of air and condensed in a tube cooled in liquid air. By direct weighing of 0.1 cu. mm. or 0.001 mgm. of this gas on the micro-balance its atomic weight (on the assumption that it is mono-atomic) was found to be 222.4. It is an inert gas belonging to the argon group. It liquefies with great sharpness between -152° and -154° : the liquid boils at -65° and solidifies at -71° . Under the microscope the liquid is colourless and transparent, whilst the solid is opaque. The liquid glows with great brilliancy in a glass tube, with a steel-blue light which at lower temperatures changes to brilliant orange-red. Ramsay proposed for the gas the name *niton* (Latin *nitidus* = shining), but **radon**, proposed by Schmidt in 1918, is now used. It has a characteristic spectrum, similar to that of xenon, and is distinctly soluble in water.

The unit of radioactivity is the *curie*, which is the activity of 0.63 cu. mm. of radon in equilibrium with 1 gm. of radium.

Ramsay and Soddy observed that radon on standing gradually lost its characteristic spectrum, whilst the helium spectrum appeared. The conversion of radon into helium was also proved by the experiment of Rutherford and Royds mentioned on p. 398. The radon changes into helium and other products, and fresh radon is produced from the radium.

The atomic weight of radium is 226, and the observed density of radon gives its atomic weight as 222.4. The difference is 3.6, roughly the atomic weight of helium. The radon is formed with one α -particle in the first step in the disintegration of radium: $\text{Ra} (226) = \alpha\text{-particle} (4) + \text{Rn} (222)$. Two gases, helium and radon are the first product from solid radium.

Theory of atomic disintegration.—Radium is an element. It has a definite atomic weight, a definite spectrum, and a definite position in the periodic table. Radium is constantly changing into helium and radon. Radon is unstable and produces helium and a solid deposit on surfaces exposed to radon. This solid **active deposit** in turn gives other products in definite stages, each stage accompanied by the emission either of α -rays, or of β -rays and γ -rays. There are eight changes passed through in succession from radium to the final inactive product, and altogether five α -particles and five β -particles are emitted. The atomic weight of radium is 226, and the five α -particles have a mass of $5 \times 4 = 20$, hence the atomic weight of the final product is $226 - 20 = 206$; hence it would seem probable that the final product is an isotope of lead. This has been confirmed.

The energy emitted by radium comes largely from the kinetic energy of the swift and massive α -particles shot from the disintegrating atoms. The hypothesis of the spontaneous disintegration of atoms was put forward by Rutherford and Soddy in 1903.

The fraction of the total number of atoms undergoing disintegration in unit time is constant; in other words, the activity diminishes exponentially with the time:

$$N_t = N_0 e^{-\lambda t}$$

where N_0 , N_t are the numbers of atoms present at the beginning and after t secs., and λ is the *disintegration* (or *decay*) *constant*. The inverse of the fraction disintegrating per unit time is called the **average life** of the element, $\tau = 1/\lambda$; it is 1.443 times the period in which half the atoms have undergone disintegration (**half-life**), $T = 0.693/\lambda$. Each radioelement is characterised by its average life, which may vary from some billionths of a second to millions of years, according to the stability of the element.

Radioactive equilibrium is a state in which a parent element produces a decay product at the same rate as the latter undergoes further change. It is a stationary state but differs from ordinary chemical equilibrium because the amounts of the different substances involved are not constant, and the changes are not reversible.

In radioactive equilibrium the amounts of parent substance and disintegration products are in the ratio of their average lives.

Radioactivity of uranium.—In 1900 Crookes found that if an ordinary uranium salt is treated with ammonium carbonate, a slight residue is left in which all the photographic activity of the uranium salt is concentrated. The solution emits α -rays, which discharge an electroscope but do not affect a photographic plate, whilst the residue emits β - and γ -rays, which are photographically active. The precipitate contains a substance called **uranium-X** (actually a mixture); on standing it

became inactive, whilst the solution regained its activity and yielded another specimen of uranium-X. Uranium can grow uranium-X.

Boltwood and Soddy (1905) found that radium is produced spontaneously from uranium, but the change is not direct. An intermediate element called **ionium** is formed, which was separated by Boltwood from the mineral carnotite. He also noticed that uranium in disintegration gives two kinds of α -particles, which suggests that there are two varieties of uranium, called **uranium-I** and **uranium-II**. U-II passes directly into ionium by emission of an α -particle, whilst U-I passes into U-X₁. From U-X₁ two products are obtained, each by emission of a β -particle, viz., U-X₂ (99.7 per cent.) and U-Z (0.3 per cent), each of which, by emitting a β -particle, passes into U-II. This is an example of a **branch chain** in disintegration. The complete series of transformations of uranium (which includes that of radium, of which uranium is the parent) is given in the table on p. 402. The table also gives the transformations in the actinium series and in the independent thorium series.

Radioactivity of thorium.—In 1902 Rutherford and Soddy found that thorium gives off an emanation which behaves as a gas. By adding ammonia to a solution of a thorium salt they found that the filtrate from the thorium hydroxide contained a very active substance, which they called **thorium-X**. After a month's time, the thorium-X had lost its activity, whilst the precipitate of thorium hydroxide recovered the activity of the original thorium salt, *i.e.* the activity lost by the thorium-X. It is now known that Th-X is formed from Th through three intermediate products, **mesothorium-I**, **mesothorium-II**, and **radiothorium**. When Th-C is reached the atoms disintegrate in two different ways. Thirty-five per cent emit α -rays, forming Th-C', which then emits β -rays, forming lead; whilst 65 per cent emit β -rays, forming Th-C'', which then emits α -rays, forming lead. No detectable rays are emitted by Ms-Th₁, so that the production of Ms-Th₂ from it is called a **rayless change**. Probably feeble β -rays are emitted.

The actinium series.—Debiere in 1899 separated from the iron group in the pitchblende residues another active substance, which he called **actinium**. The immediate parent of actinium is **protoactinium**, formed by a β -ray change from an isotope of U-X₁ called uranium-Y. Protoactinium gives actinium by emission of an α -particle. Protoactinium, although an element of Group V, is chemically similar to thorium and zirconium in Group IV rather than tantalum, and accumulates in the zirconium phosphate in the residues from the pitchblende. Protoactinium pentoxide is a heavy white powder with feebly basic properties. The final product of the actinium series is an isotope of lead, of atomic weight 207.

The position of radio-elements in the periodic table.—The position of an element in the periodic table is fixed by its atomic number, equal to the positive charge on the nucleus of the atom in terms of the electronic charge as unit. The atomic numbers of uranium, thorium and radium are known from the positions of these elements in the periodic table (p. 368), and the atomic numbers of all disintegration products may be calculated by subtracting 2 for each α -particle emitted

(loss of charge +2), or adding 1 for each β -particle emitted (loss of charge -1). The positions of the disintegration products are governed by a simple rule (Russell, Soddy, and Fajans, 1913). In an α -ray change (in which an α -particle is expelled from the atom) the product falls into a group of the periodic table *two places lower* than that of the parent element. In a β -ray change (in which an electron is expelled from the atom) the product falls into a group *one place higher* than that of the parent element.

Radium, in the second group, emits an α -particle and forms radon, an inert gas of the zero group: RaD (an element of Group IV) emits a β -particle and forms RaE, an element of Group V.

The three main series of radio-active elements are shown in Fig. 235, in which their positions in the periodic table are evident. More than

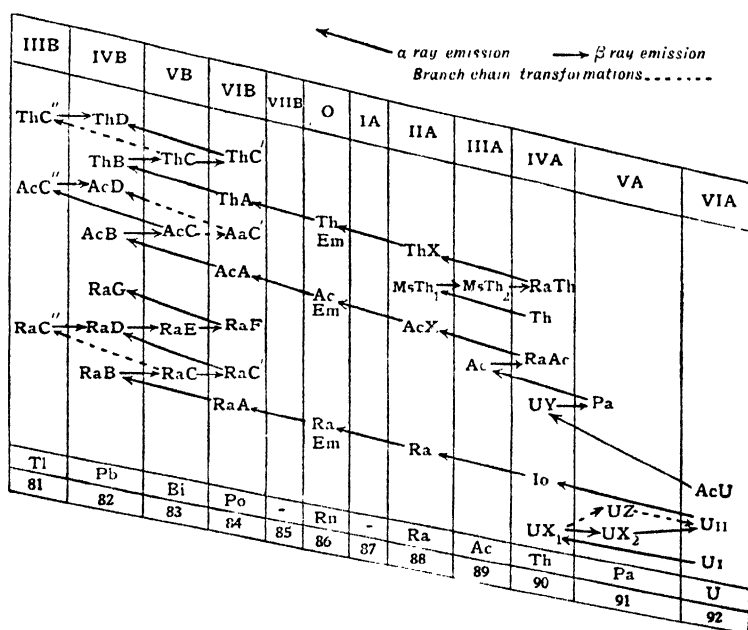


FIG. 235.—Radioactive Series.

one kind of atom may occupy the same place, specified by the atomic number given at the foot of the table, and these different kinds of atoms are isotopes (see p. 382); they are inseparable one from another by ordinary chemical processes but may be distinguished by their rates of disintegration and the nature of the elements from which they are derived or of the products to which they give rise. Isotopes are differentiable by their atomic weights and their densities, since the atomic volumes are identical.

The molecular solubilities of common lead nitrate and of uranio-lead nitrate are 1.7993 and 1.7991 gm. mol. per litre, respectively. The actual

weights of lead per 100 gm. of water are 37.281 and 37.130, substantially in the ratio of the atomic weights.

The X-ray spectra of ordinary lead and of uranium lead, which depend only on the atomic number, are identical within the error of 0.0001 Å. The spectra differ by about 0.005 Å., which is measurable (Merton, 1919).

Radioactive elements not included in the series of Fig. 235 include isotopes of potassium and rubidium in Group I, showing feeble β -ray activity, and of samarium in Group III, showing feeble α -ray activity, and also the transuranic elements with atomic numbers higher than that of uranium (p. 407).

The tendency of workers on radioactivity was to regard isotopes as different elements, but since they are identical in chemical properties, Paneth (1916) suggested that they should be regarded as varieties of elements. Perhaps the most satisfactory definition, closely related to Moseley's law (p. 394), is that an element is defined by its atomic number. The discovery of non-radioactive isotopes such as hydrogen and deuterium, which are readily separated and have widely different properties, has made this problem rather more difficult than was suspected. Cases of different radioactive elements with the same atomic number and mass are also known.

Deflexion of α -rays in gases.—The α -particles passing through air produce gaseous ions which can act as centres for deposition of moisture. In a vessel of air saturated with moisture and suddenly cooled by expansion, the paths of the rays become visible in lines of droplets of water condensed on the ions, which can be photographed. In this way

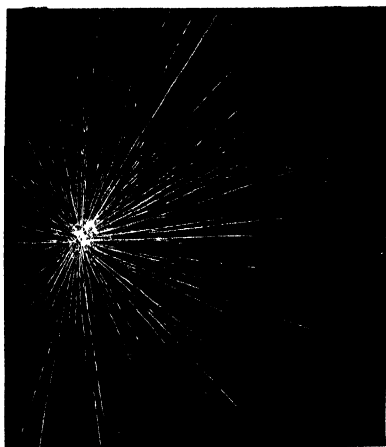


FIG. 236.—Tracks of α -rays.

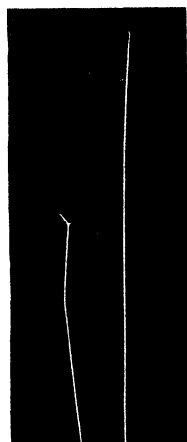


FIG. 237.— Tracks of two α -rays (enlarged).

C. T. R. Wilson obtained the photograph shown in Fig. 236. The paths of two single α -rays are shown in Fig. 237. It is seen that they end abruptly. The α -particle must have passed through several gas atoms without suffering appreciable deflexion, but the left-hand track shows a

large deflexion at its end, and a very small spur going off in the other direction. The latter represents the track of the gas atom which stopped the α -particle; this had imparted to it a recoil velocity, and the angle between the track and the original direction of the α -particle gives the relative masses of the striking and struck particle, in agreement with the laws of elastic collision (oxygen 16.72 ± 0.42 ; helium 4.03). The method gives a means of determining the masses of single atoms (Blackett, 1922).

The structure of the atom.—The abrupt and often large deflexion of the α -particle at the end of its track suggests that its positive charge approached very close to some positive charge in an atom of gas, a large repulsive force arising between the two like charges. As the α -particle passed through several atoms without deflexion, this positive atomic charge must be concentrated in a small volume compared with the volume of the atom. Calculation from the deflexions by the inverse square law shows that the two charges approach within a distance of 10^{-12} cm., whereas the radius of an atom is of the order of 10^{-8} cm.

The atom is electrically neutral, and in addition to the positive nucleus it must contain negative electrons. Rutherford in 1911 assumed that it consists of a small positive nucleus surrounded by electrons revolving about the nucleus, the diameter of the outer orbit being the diameter of the atom. The greater part of the atom is empty space. The electrons have a very small mass, so that the mass of the atom is concentrated in the positive nucleus.

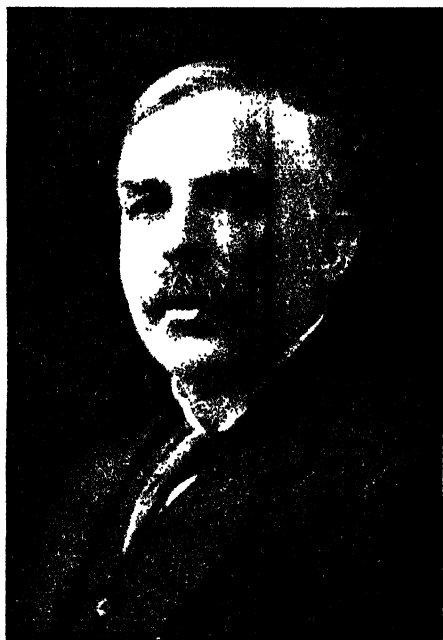
The hydrogen atom was assumed by Bohr (1913) to consist of a nucleus of charge +1 (the proton, p. 224), with one electron of charge -1 revolving around it in a circular orbit. The nucleus of the helium atom (mass 4) has a charge (and atomic number) of 2, and is identical with the α -particle. In the helium atom there are two electrons outside the nucleus.

The series of atomic numbers suggests (van den Broek, 1913) that successive atoms counting from hydrogen have nuclei containing one additional positive charge for each step in atomic number. This is confirmed by the deflexion of α -rays by various atoms.

By measuring the scattering of α -particles passing through thin sheets of metal, Chadwick (1920) calculated the charge on the nucleus of the metal atom, on the assumption that the deflexions were caused by the approach of the positive helium nuclei towards the positive nuclei of the atoms. For platinum, silver, and copper the nuclear charges were found to be 77.4, 46.3, and 29.3, in very good agreement with the atomic numbers 78, 47 and 29, of these elements. The number of scattered α -particles was counted by the scintillation method (p. 125).

In chemical changes only the outer electrons are disturbed. The shift of outer electrons from one orbit to another is supposed to give rise to radiation emitted by the atom, *i.e.* to its spectrum. It is only in radioactive changes, or in changes brought about by fast α -particles, hydrogen or deuterium nuclei, neutrons, or γ -rays, entering the atom, that the nucleus of the atom is affected (p. 406).

In the atom there are two distinct regions—the nucleus and the outer electrons. The nucleus is exceedingly small in comparison with the size of the atom, and *the positive nuclear charge is equal to the atomic number of the element*. The outer negative electrons in the neutral atom balance the positive charge of the nucleus, or are n fewer or greater in the case of the n -valent positive or negative ion. The electrons are situated at relatively great distances from the nucleus, and in the heavier atoms they are arranged in several shells or orbits. Recent



Russell, London.

LORD RUTHERFORD.

theory regards Rutherford's picture of electrons revolving around a nucleus as too simple, but the idea of shells (or energy levels) is retained.

Since the mass of the α -particle or helium nucleus is 4 and its charge is +2, it is assumed to be composed of 2 protons (mass 1, charge +1) and 2 neutrons (mass 1, charge 0). The nuclei of heavier atoms are supposed to be built up from p protons and n neutrons, so that the mass is $p+n$ and the charge p . The charge is equal to the atomic number. The nuclei of the three isotopes of oxygen, of masses 16, 17 and 18, have the same charge +8, equal to the atomic number, and contain 8 protons. In addition they contain 8, 9 and 10 neutrons, respectively.

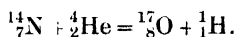
The transmutation of elements.—Although the rate of disintegration of the atoms of radioactive elements cannot be influenced by any known means, the collision of swift α -particles, protons (hydrogen nuclei), deuterons (deuterium nuclei), neutrons, or γ -rays, with atoms of other

elements can cause the disruption of the atomic nuclei, leading to the ejection of fragments of the atom with such velocities that their presence may be detected by the scintillation method.

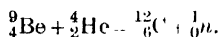
Rutherford in 1919 extended an observation by Marsden (1914), according to which the protons (H-nuclei) ejected by the α -particles of Ra-C by collision with hydrogen atoms had a range of about 28 cm. in air as determined by the scintillation method on a zinc sulphide screen, whilst the range of the α -particle is about 7 cm. The identity of the long range particles with H-nuclei was established by the measurement of *c.m.* by deflexion in electric and magnetic fields.

Rutherford, partly in collaboration with Chadwick, showed that long range protons are also produced by the bombardment of boron, nitrogen, fluorine, sodium, aluminium and phosphorus by α -rays, and thus provided a proof that the nuclei of these atoms contain H-nuclei or protons, and at the same time gave the first definite case of artificial disintegration of an element. The number of atoms disintegrated is exceedingly small.

Blackett (1922) by the Wilson method (p. 403) obtained photographs of collisions involving the expulsion of protons from atoms. When α -particles (mass 4; nuclear charge 2) bombard nitrogen atoms (mass 14; nuclear charge 7) they apparently enter the nucleus of the atom, producing a particle of mass $14 + 4 = 18$ and nuclear charge $7 + 2 = 9$, *i.e.* an isotope of fluorine (atomic number = 9). This nucleus emits a proton (mass 1; charge 1), leaving a nucleus of mass $18 - 1 = 17$ and charge $9 - 1 = 8$, *i.e.* an isotope of oxygen (atomic number = 8). The branch at the end of the α -ray track shows only two prongs, corresponding with the H-particle and the new nucleus. This is an example of the artificial building up of an element (oxygen) from a lighter element (nitrogen), and is represented as follows, the lower figures giving the charges, and the upper the masses, of the nuclei:



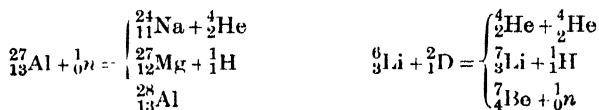
In what follows we denote the neutron by ${}_{0}^{1}\mu$, the negative electron by β^{-} , and the positive electron (positron) by β^{+} . D and T denote deuterium (${}^2\text{H}$) and tritium (${}^3\text{H}$) nuclei. Neutrons are formed by the action of α -rays on beryllium, when presumably carbon is also produced:



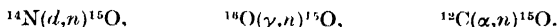
Some examples of nuclear transformations are:



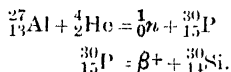
In some cases alternative changes may occur:



Nuclear transformations may be shown by the symbols of the initial and final nuclei separated by brackets containing the symbols of the impacting and emitted particles in this order, α , p , d , n , and γ denoting the alpha-particle (or artificially accelerated helium nucleus), proton, deuteron, neutron, and γ -ray :

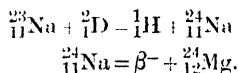


Joliot and Mme Curie-Joliot in 1934 observed that in some cases a bombarding particle is absorbed by the nucleus, producing an unstable atom which then disintegrates with emission of a positron. The unstable atom behaves as an artificial radioactive element with a characteristic half-life. In the bombardment of aluminium with α -particles, the helium nucleus enters the aluminium nucleus, forming an unstable isotope of phosphorus, which then disintegrates with the emission of a positron, forming an isotope of silicon:

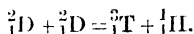


The radioactive-phosphorus ${}^{30}_{15}\text{P}$ has a half-life of 3 minutes and its intermediate formation is confirmed by its co-precipitation from a solution of the irradiated aluminium along with the common isotope, *e.g.* as zirconium phosphate, when the precipitate shows radioactivity with the definite period of decay.

Radio-sodium with a relatively long life and giving off intense β^- and γ -rays is obtained by bombarding sodium chloride with high-energy deuterons :

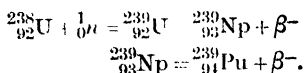


A radioactive isotope of hydrogen of mass 3 (*tritium*) is formed by collision of deuterium nuclei :



The number of artificial elements has since swelled to very large proportions. Some elements not known in nature (*e.g.* those with atomic numbers 43, 85 and 87) can be so produced, but the most spectacular result is the synthesis of elements with atomic numbers and atomic weights higher than those of uranium (atomic number 92).

Transuranic elements.—Natural uranium consists mostly of the two isotopes ${}^{238}\text{U}$ (99.3 per cent) and ${}^{235}\text{U}$ (0.7 per cent). When ${}^{238}\text{U}$ is bombarded with neutrons it is converted into two new elements with atomic numbers 93 and 94 called **neptunium** (Np) and **plutonium** (Pu), respectively (named after the planets Neptune and Pluto) :



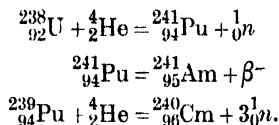
Neptunium and plutonium isotopes are formed by several other nuclear reactions.

The isotope ${}^{235}\text{U}$ when bombarded with neutrons undergoes fission into two parts, radioactive isotopes of barium and krypton, and more neutrons

are emitted so that an atomic chain reaction is set up. Owing to the loss of total mass in the process a vast amount of energy is omitted. This is the principle of the atomic bomb. Plutonium may undergo fission and produce an atomic explosion.

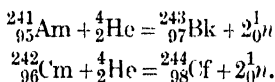
The isotope ^{235}U , called *actinouranium*, is the parent of U-Y (Fig. 235).

Bombardment of ^{238}U and ^{239}Pu by very high energy helium ions forms two radioactive elements of atomic numbers 95 (americium, Am) and 96 (curium, Cm), which seem to belong to Group III :

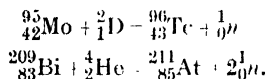


Americium and curium isotopes are formed by other nuclear reactions.

Two radioactive elements of higher atomic numbers, **berkelium** Bk (at. no. 97) and **californium** Cf (at. no. 98) are formed by bombarding americium and curium, respectively, with high-energy helium ions :



Isotopes of elements no. 43 and 85 have been obtained by bombarding molybdenum with deuterons, and bismuth with α -particles, respectively, and are called **technetium** (Tc) and **astatine** (At), respectively :



CHAPTER XXIV

THE STRUCTURE OF THE ATOM; COORDINATION COMPOUNDS

The structure of the atom.—Dalton and chemists generally throughout the nineteenth century regarded the atom as a kind of minute, hard billiard ball, incapable of division, all the atoms of a given element being exactly alike. The discovery of isotopes disproved the second assumption. Ever since Prout in 1816 suggested that all elements are formed from the lightest element, hydrogen, chemists suspected that atoms might be divisible into simpler parts, though what these parts were or how the division was to be made no one knew. With the discovery of radium by Madame Curie in 1898, and the investigation of radioactivity, it became possible to explore the inner structure of the atom.

The atom of hydrogen was pictured by Rutherford as consisting of a very small positively charged nucleus, outside which and at a considerable distance from it is a negative electron which neutralises the charge of the nucleus. The nucleus of the hydrogen atom is called the **proton**. An uncharged particle called the **neutron**, of the same mass as the hydrogen nucleus, is also known. The nuclei of atoms heavier than hydrogen are supposed to be built up of protons and neutrons; the number of protons is equal to the positive charge of the nucleus, which is equal to the atomic number; the sum of the protons and neutrons corresponds with the atomic mass. Outside the nucleus are as many electrons as there are protons in the nucleus. Since isotopes have the same atomic number, their nuclei have the same number of protons but different numbers of neutrons.

In Rutherford's theory and its development by Bohr (p. 427) the electrons were supposed to be revolving around the nucleus in orbits, like planets around the sun. The newer developments of atomic theory, involving the wave theory of the electron (p. 435), have modified this picture, and the idea of point charges (electrons) revolving in definite orbits is no longer entertained.

The next atom to hydrogen, helium, is supposed to have a nucleus of mass 4 and charge 2, composed of two protons and two neutrons. Outside this nucleus are two electrons. In still heavier atoms the two electrons of the helium atom are retained in an inner shell next to the nucleus, and successive atoms in the periodic table may be supposed to be built up as follows.

The positive charge of the nucleus increases by 1 unit for each successive step in atomic number. The mass of the nucleus increases, usually by more than 1 unit, by addition of protons and neutrons. The

structures of the atoms from hydrogen to neon can then be represented as follows :

	<i>Mass of nucleus</i>	<i>Charge on nucleus</i>	<i>Outer electrons</i>
H	1	1	1
He	4	2	2
Li	7	3	2 + 1
Be	9	4	2 + 2
B	11	5	2 + 3
C	12	6	2 + 4
N	14	7	2 + 5
O	16	8	2 + 6
F	19	9	2 + 7
Ne	20	10	2 + 8

When a 2-electron shell is completed with helium, a new shell begins to be formed containing from 1 electron in lithium to 8 electrons in neon. The structures of the next period of atoms higher than neon is a repetition of this, a new shell of 8 electrons being completed with the next inert gas, argon. *The outer shells of all the inert gases contain 8 electrons*, and this stable grouping of an **octet of electrons** suggests an arrangement at the corners of a cube (G. N. Lewis, 1916). In Fig. 238 the inner shells

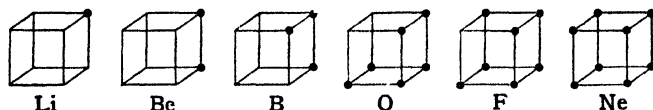


FIG. 238.—Structure of atoms on the octet theory.

are supposed to be inside the cubes, only the outer electrons being shown.

The eight elements in periods 2 and 3 correspond with the completion, step by step, of two successive shells of 8 electrons around the nuclei : the positive charges of the nuclei increase in steps of 1 unit from one element to the next. Periods 4 and 5 contain 18 elements each, so that it is supposed that shells of 18 electrons are completed. Since the outer shells of krypton and xenon each contain 8 electrons, there must be completed shells of 18 electrons below them, the original outer shell of 8 in the case of argon and krypton thus expanding to 18. The electronic structures of the inert gases are therefore :

He	-	-	-	2
Ne	-	-	-	2 + 8
Ar	-	-	-	2 + 8 + 8
Kr	-	-	-	2 + 8 + 18 + 8
Xe	-	-	-	2 + 8 + 18 + 18 + 8
Rn	-	-	-	2 + 8 + 18 + 32 + 18 + 8

Period 6 contains 32 elements, hence 32 electrons are added in succession in passing from xenon to the radioactive emanation. In passing through the series of rare earths, the *inner* group of 18 elec-

lithium ion has the electron pair of the helium atom as its outer shell, whilst the fluorine ion has an outer octet of electrons like neon. The transfer of the electron gives rise to the charges of the ions. The chlorine atom has an inner octet (the neon structure) and 7 outer electrons. On reaction with a sodium atom, with an inner completed octet and 1 outer electron, the sodium loses 1 electron and the chlorine gains 1 electron, the ions Na^+ and Cl^- being formed, each with the complete external octet of argon. In such compounds as Li^+F^- and Na^+Cl^- there is no true valency bond between the ions, these being held by electrostatic attraction in the lattice whilst in solution the ions are free. Such a link is sometimes called an **electrovalent link** or an **electrovalency**.

Lewis assumed that *in the formation of an ordinary single valency bond (covalent link or covalency) a pair of electrons is shared in common by two atoms*. In this way one or both atoms may complete an octet of electrons. The water molecule is formed from an oxygen atom with 6 outer electrons and two hydrogen atoms each with 1 electron, and the oxygen in water is surrounded by 8 electrons (Fig. 239). The formation of a chlorine molecule from two atoms of chlorine, each with 7



FIG. 239.---Water molecule.

outer electrons, may be represented by two cubes joined along an edge, this edge having a shared pair of electrons and representing the single bond (Fig. 240). If the outer electrons are represented by dots, each

atom of chlorine will be: $\cdot\ddot{\text{Cl}}\cdot$ and the chlorine molecule will be: $\cdot\ddot{\text{Cl}}:\ddot{\text{Cl}}\cdot$ which is the electronic formula corresponding with the structural formula $\text{Cl}-\text{Cl}$. In this case each chlorine is surrounded by an octet of electrons. It should be noted that the chemical symbol Cl now represents the atomic nucleus plus the completed shells (2 + 8) of inner electrons other than valency electrons this is called the **atomic core**.

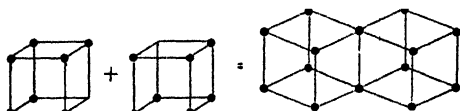
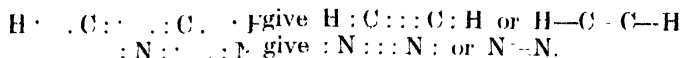


FIG. 240. - Formation of chlorine molecule.

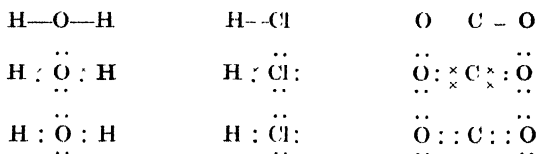
A **double bond** is formed by four equally shared electrons, two from each atom, *i.e.* two shared pairs of electrons. Fig. 241 shows the formation of carbon dioxide from $\text{C} + 2\text{O}::\text{O}::\text{C}::\text{O}$: the double bonds in $\text{O}=\text{C}=\text{O}$ each having four electrons.

A **triple bond** is formed by six equally shared electrons, three from each atom, or three shared pairs:



It must be remembered that the octet representation is pictorial and the arrangement of electrons outside the core is not necessarily cubical.

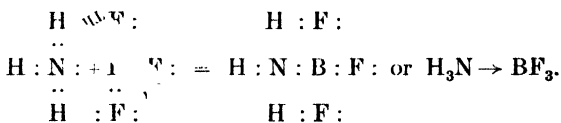
Electrons which belonged to different atoms may for clearness be distinguished by using crosses, etc., but in the resulting bond there is no difference between the electrons :



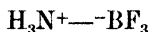
When the pair of electrons required to form a covalent link comes from *the same atom* instead of being provided by and equally shared between two atoms, a **coordinate link** is formed. Coordinate links are formed when apparently saturated molecules add on other molecules to form what were called "molecular compounds".

Boron has 3 electrons in the outer shell and can share these with 3 fluorine atoms, forming the saturated compound boron trifluoride BF_3 , in which the boron is surrounded by 6 electrons. Nitrogen

has 5 outer electrons and shares 3 with three hydrogens forming ammonia NH_3 , with an outer octet around the nitrogen. Of this octet 2 electrons form a *lone pair*, i.e. are unshared. This pair may be *donated* to the boron atom in BF_3 , so raising the number of electrons round the boron from 6 to 8. The resulting link may be denoted by an arrow instead of a line :



Actual measurements show that this type of link is longer than an ordinary covalent link. Since the shift of charge in the molecule leaves the nitrogen with a smaller share of negative electronic charge than the boron, the link may be denoted by



and, (as it has some character of a covalent bond and some of an electrovalent link) it has been called a *semipolar double bond* or *co-ionic link*. For this reason ammonia adds to many metallic salts, forming what are called **coordination compounds**, e.g. $\text{Co}(\text{NH}_3)_6\text{Cl}_3$. The number of groups coordinated with the metal atom (**coordination number**) is usually 4 or 6. The atoms or groups attached to the metal (or other "central" atom) in coordination compounds are attached by **co-valencies** and are not ionisable ; those "outside" the complex nucleus

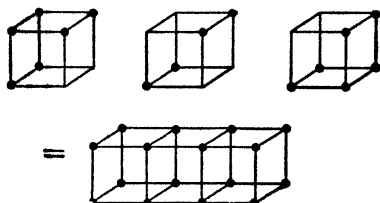
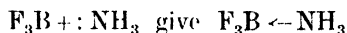


FIG. 241.--Formation of carbon dioxide.

Coordinate links or semi-polar double bonds ; formed by pairs of electrons contributed by *one* of the atoms :



Solid crystals may consist of (a) **ionic lattices** (salts) ; (b) **molecular lattices** e.g. solid O_2 , N_2 , CO, NO, $CH_3 \cdot CH_3$, in which the intermolecular forces (between the molecules) are different from the intramolecular forces (between the atoms) ; these are usually non-conductors of electricity and relatively volatile ; (c) **layer lattices** made up of large ions each associated with two small ions forming practically electrically neutral layers held together by weak non-polar forces and easily split into thin sheets (e.g., CdI_2 , $Mg(OH)_2$, etc.) (Fig. 242c) ; (d) **metals** and

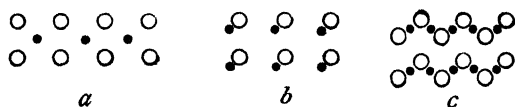
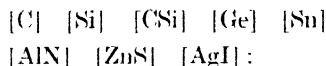


FIG. 242.—Types of lattices

their compounds with one another : [Na], [Cu], [Cu₂Mg], perhaps [Pd₂H], in which there is probably no difference between intermolecular and intramolecular forces ; they are difficultly volatile and conductors ; (e) according to Grimm and Sommerfeld, solid elements in Group IV, or binary compounds of elements from two groups equidistant from Group IV on opposite sides, form atomic lattices with tetrahedral linkages, as in the diamond lattice (p. 391) :



these are mostly non-volatile, hard, and non-conductors ; (f) in crystals of solid argon or of other inert gas atoms the intermolecular forces are identical with the intramolecular forces, as in salts and metals, but are non-polar.

The distinction between **ionic or polar** (*dualistic*) and **covalent or non-polar** (*unitary*) compounds is evident from X-ray analysis (e.g. $NaCl$; diamond) ; by residual rays ; by optical activity or special kinds of stereoisomerism which necessitate directed covalent (non-polar) bonds ; by colour, etc. (e.g. ionisation of a polar salt produces little change of colour). In polar compounds the sum of the outer electrons is 8 or a multiple of 8 (e.g. $NaCl$) but not in non-polar compounds ($F : F$; i.e. 14).

Abegg distinguished the polar character of an element by : (1) ionisation, e.g. $HCl \rightarrow H^+ + Cl^-$; (2) hydrolysis, e.g. $P_2N_5 + 12H_2O \rightarrow 3H_4P^+O_4 + 5NH_3^-$; (3) position in the periodic table as compared with that of other elements with which it combines, e.g. S_2Cl_2 ; (4) the formulae of compounds in which it exerts its maximum valency. The last criterion is based on Abegg's

theory that an element has a normal valency and a contravalency, the sum of which is equal to eight :

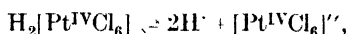
Group	-	-	I	II	III	IV	V	VI	VII
Normal valency	-	+1	+2	+3	± 4	-3	-2	-1	
Contra-valency	-	(-7)	(-6)	(-5)		+5	+6	+7	

E.g., S in H_2S^{2-} and S^{6+}O_3 . If we represent the compound $\text{BF}_3\cdot\text{NH}_3$ with a semipolar double bond, we see that the boron atom has a valency of -5.

COORDINATION COMPOUNDS

Werner's theory.—The formation of $\text{BF}_3\cdot\text{NH}_3$ from the two molecules BF_3 and NH_3 , neither having free valency in the usual sense, is explained by the formation of a covalent bond between N and B by the donation of the lone pair of electrons of the nitrogen to form a coordinate bond (dative bond ; semipolar double bond) : $\text{F}_3\text{B} \leftarrow \text{NH}_3$, a type of linkage believed to be present in large groups of so-called **coordination compounds**, first systematised by Alfred Werner (1893).

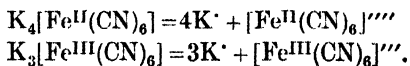
The saturated molecules PtCl_4 and 2HCl combine to form a stable dibasic acid H_2PtCl_6 , capable of ionisation and of forming salts such as K_2PtCl_6 , in which the chlorine is not ionisable but is firmly bound to the metal atom, silver nitrate giving Ag_2PtCl_6 , not silver chloride. Werner represented H_2PtCl_6 (the valency of the metal being shown by a roman numeral) as :



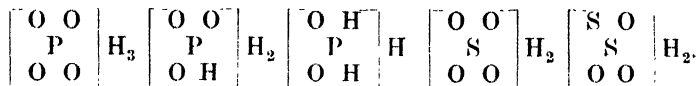
the group in square brackets forming a complex nucleus. The compound PtCl_4 also combines with ammonia to form $\text{PtCl}_4(\text{NH}_3)_2$, which has no properties of a salt but behaves as a neutral molecule ; it gives no reactions for Pt^{2+} or Cl^- ions and forms a non-conducting solution. It is an unchanged nucleus : $[\text{PtCl}_4(\text{NH}_3)_2]$. In the stable compounds containing trivalent cobalt and ammonia (**cobaltamines**), and in the cobaltinitrites, the cobalt atom is also associated in the nucleus with six atoms, radicals, or neutral molecules :

- (a) $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3 = [\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$
- (b) $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} = [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$
- (c) $[\text{Co}^{\text{III}}(\text{NO}_2)_6]\text{K}_3 = 3\text{K}^+ + [\text{Co}(\text{NO}_2)_6]^{3-}$

In compound (b) only one-third of the chlorine is ionisable and exists as ions bound to the positive nucleus by electrostatic forces, like the ions in salts ; the rest of the chlorine is firmly bound to the metal atom in the nucleus by covalencies. In a similar way, ferro- and ferri-cyanides contain cyanogen radicals attached by covalencies to the iron atoms in the nuclei and show none of the reactions of iron or cyanides :

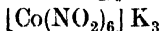
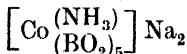
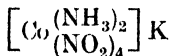
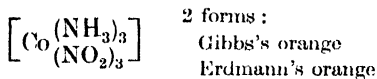
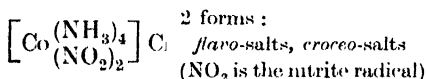
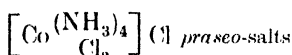
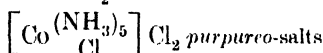
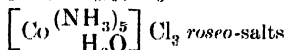
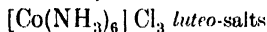
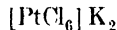
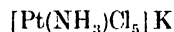
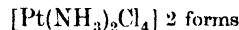
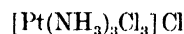
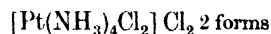
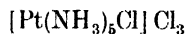
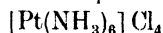
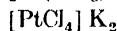
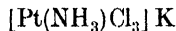
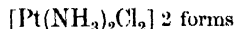
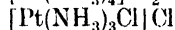
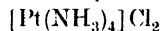


Although in most cases the central atom in the nucleus is a metal, non-metallic compounds may be similarly represented, *e.g.* with P^V and S^{VI}:

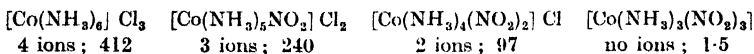


The atoms or radicals in the nucleus are said to be **coordinated** with the central atom, and since they are not ionisable must be attached by covalencies. The number of such groups, which is often six, but may be four as in $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$, and sometimes eight as in $[\text{Mo}(\text{CN})_8]\text{K}_4 + 2\text{H}_2\text{O}$ and $[\text{W}(\text{CN})_8]\text{K}_4$, is called the **coordination number**.

Tervalent cobalt and quadrivalent platinum have the coordination number six; bivalent platinum has the coordination number four.

Compounds of Co^{III}Compounds of Pt^{IV}Compounds of Pt^{II}

The existence of isomeric forms of some types is mentioned. That the formulae correctly represent the numbers of ions formed is shown by the molecular conductivities at equal concentrations:



Valency rule for coordination compounds.—An examination of the formulae given above shows that (i) *the electrovalency of the nucleus is equal to the positive valency of the metal or other central atom when this is coordinated only with neutral molecules such as NH₃ or H₂O*; (ii) *if*

negative radicals such as Cl, NO₂, or CN, which may be regarded as ions, are in the nucleus, the positive valency of the central atom is reduced by one unit for each unit of electrovalency present, and if the negative valency of these radicals exceeds the positive valency of the central atom, the nucleus as a whole becomes negative and is associated with a corresponding number of positive ions outside. For example :

[Pt^{IV}(NH₃)₄(Cl₂)] has a valency of 4 - 2 = 2 and forms [Pt(NH₃)₄(Cl₂)Cl₂].

[Pt^{IV}(NH₃)Cl₅] has a valency of 4 - 5 = - 1 and forms [Pt(NH₃)Cl₅]K.

[Fe^{III}(CN)₆] has a valency of 3 - 6 = - 3 and forms K₃[Fe(CN)₆].

[Fe^{II}(CN)₆] has a valency of 2 - 6 = - 4 and forms K₄[Fe(CN)₆].

[Co^{III}(SO₄)(NH₃)₅] has a valency of 3 - 2 = 1 and forms [Co(NH₃)₅SO₄]Br.

[Co^{III}(NH₃)₅Br] has a valency of 3 - 1 = 2 and forms [Co(NH₃)₅Br]SO₄.

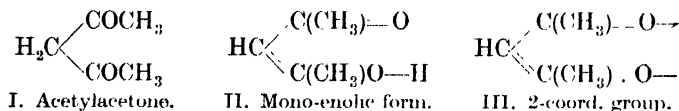
The last two compounds are isomeric ; the first behaves in solution as a bromide, the second as a sulphate.

Positive and negative nuclei may also form salts with each other, e.g., [Cr(NH₃)₆][Cr(SCN)₆], with valencies of + 3 and - 3, respectively.

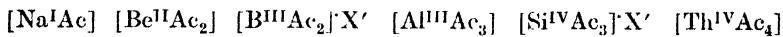
Multi-coordinating groups.—In some cases groups may occupy two, three, or four coordination positions.

(i) *2-coordinating groups* (formerly called *chelate groups*) are : ethylenediamine NH₂·CH₂·CH₂·NH₂, represented by en : αα'-dipyridyl (dipy) : radicals such as C₂O₄'', CO₃'', SO₃'', SO₄'', and the radicals of acetylacetonone and dimethyl glyoxime. In the last two cases the group has one principal valency (due to loss of H from the compound) and one coordinate link is formed by the oxygen and nitrogen, respectively, by donation of a pair of electrons to the shell of the central atom to which the group is attached.

(a) In the case of *acetylacetonone* the radical is produced from the tautomeric mono-enolic form :

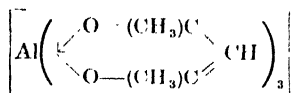


Compounds of acetylacetonone with elements having coordination numbers of 2, 4, 6 and 8 are known :

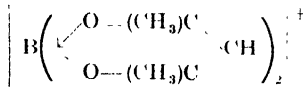


Compounds similar to [AlAc₃] are formed with trivalent Ga, In, Sc, Y, Ce, V, Mn, Co, and are all covalent. With boron and silicon, ions are formed.

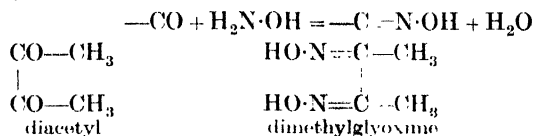
The combination of three molecules of acetylacetonone radical with an aluminium atom may be explained thus. The Al has three valency electrons which it shares with the electrons on the three lower oxygens of formula III above to form three single covalent links. The three upper oxygens form three coordinate links by donating three pairs of electrons, so that the aluminium is surrounded by a group of 12 electrons (covalency = 6) and a neutral molecule is formed :



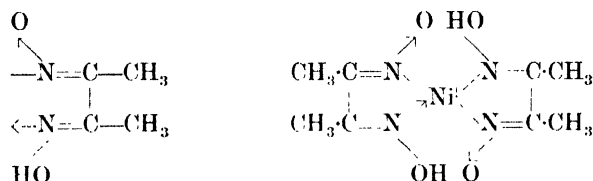
In the case of boron, two molecules of acetylaceton radical are linked to the atom, giving $2 + 4 = 6$ electrons. The boron has 3 electrons, and this would make a shell of 9. The stable shell, for an element of the second period, is 8, hence one electron is lost, forming a positive ion :



(b) The so-called *glyoximes* are oximes of the diketone diacetyl, formed by reaction of hydroxylamine with the two keto-groups :

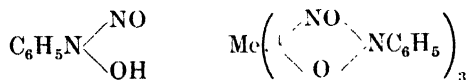


One $=\text{N}\cdot\text{OH}$ group loses a hydrogen atom and the radical attaches to a metal atom such as nickel by sharing an electron on the nitrogen and forming a covalent bond, whilst the other $=\text{N}\cdot\text{OH}$ group is attached by an electron pair on the nitrogen forming a coordinate link :

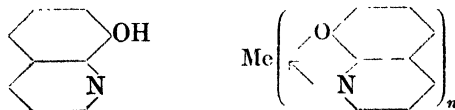


The valencies are all in a plane and *cis-trans*-isomers (p. 423) can be formed according to the orientation of the two rings (Chugaev, 1910). It should be noted that the attachment is through the nitrogen, not through the oxygen, since similar compounds are formed if $-\text{NOH}$ is replaced by $-\text{NH}$ or $-\text{NC}_6\text{H}_5$.

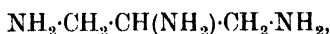
A reagent behaving like dimethylglyoxime is *cupferron*, the ammonium salt of nitrosophenylhydroxylamine, which precipitates, e.g. ferric iron :



The important reagent *oxine* is 8-hydroxyquinoline, precipitating many metals as $\text{Mc}(\text{C}_9\text{H}_6\text{ON})_n$, where n is the valency of the metal :

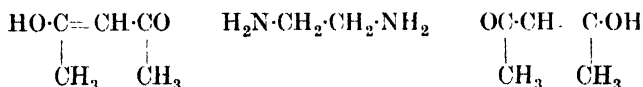


(ii) A 3-coordinating group is $\alpha\beta\gamma$ -triaminopropane (=tp):

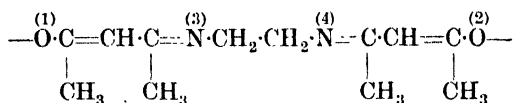


which forms compounds, by donation from the three nitrogens, with Co^{III} , Rh^{III} , etc. (Pope and Mann, 1926): $[\text{Co tp}_2]\text{Cl}_3$, $[\text{Rh tp}_2]\text{Cl}_3$, in which tp_2 occupy six coordination positions.

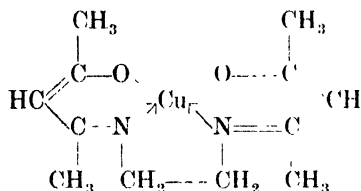
(iii) A 4-coordinating group is the enolic radical of ethylene diamino-bisacetylaceton (=ec), formed by condensing two molecules of the enolic form of acetylaceton with a molecule of ethylenediamine:



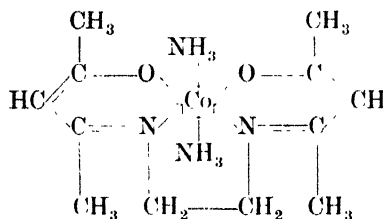
and loss of two hydroxyl hydrogens:



This attaches at (1) and (2) by electron-sharing to form ordinary covalencies and at (3) and (4) by electron donation to form coordinate links. The very stable cupric compound (Cu^{II} ec):



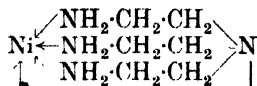
was prepared by Combes (1889). The cobaltic compound can add 2NH_3 to complete the coordination number 6 in $[\text{Co ec}(\text{NH}_3)_2]^+$:



Another 4-coordinating group is $\beta\beta'\beta''$ -triaminotriethylamine



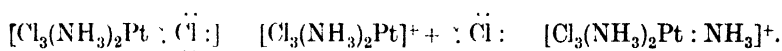
(=tren), forming $[\text{Ni tren}]\text{SO}_4$, $[\text{Pt}^{\text{II}} \text{tren}]\text{I}_2$ (Mann 1926), with a tetrahedral arrangement of valencies:



Coordination and stability.—Coordination often increases the stability of compounds in a marked degree. Whereas trivalent cobalt is unstable in its simple compounds, the cobaltamines are very stable. Cuprous nitrate forms a stable compound with methyl cyanide, $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4]\text{NO}_3$. Cupric iodide forms stable coordination compounds such as $[\text{Cu}^{\text{II}}(\text{NH}_3)_6]\text{I}_2$. Coordination compounds of bivalent silver are, e.g. $[\text{Ag}^{\text{II}}(\text{dipy})_2]\text{X}_2$ (dipy = $\alpha\alpha'$ -dipyridyl, X = univalent acid radical).

Electronic theory of coordination.—Coordinate links, which always behave as covalencies, are formed by the donation of a pair of electrons by an atom possessing a lone pair, such as nitrogen and oxygen, in the addenda (NH_3 , H_2O , etc.), each bond so formed introducing two electrons to the shell of the central atom but not altering the electric charge, since the added molecule is neutral.

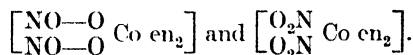
Electrovalencies are produced by such processes as the following: from $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$, a neutral complex in which the atoms and groups are united by covalencies, let one Cl be removed as an *ion*, taking one electron from the shell of the metal to form Cl^- : and leaving a positive charge on the metal. The *pair* of electrons so lost is then supplied by donation from a neutral NH_3 molecule added:



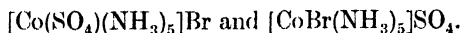
A distinction is sometimes made between the *coordination number* and the *covalency* of the central atom. These are equal only when all the covalencies are single and there are no electrostatic links, but when double or triple bonds occur between the central atom and atoms or groups attached to it, the coordination number is less than the covalency.

Isomerism of complex compounds.—Several types of isomerism are predicted by Werner's theory:

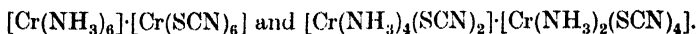
(1) *Structural isomerism in the nucleus*, e.g.:



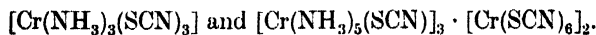
(8) *Ionisation isomerism*, in which positions inside and outside the nucleus are interchanged, e.g.



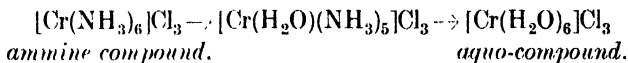
(3) *Coordination isomerism*, depending on the different arrangements of groups in two nuclei in combination:



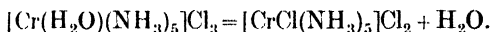
(4) *Coordination polymerism*:



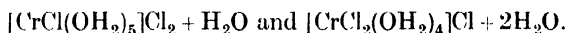
(5) *Hydration isomerism*: the groups NH_3 , Cl , etc., in the nucleus may be replaced by water, H_2O , forming *aquo-compounds*:



In such compounds, part of the ionisable Cl may pass into the nucleus and then ceases to be ionisable:



The two green chromic chlorides are isomeric compounds of this type:

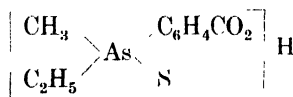


The blue modification is $[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$.

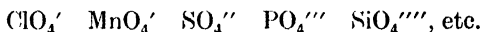
(6) *Geometrical isomerism*, due to the different arrangement of the atoms and groups in space about the central atom.

(a) *Coordination number 4*. Two cases are possible:

(i) *Tetrahedral arrangement of valencies*. This is found with 4-covalent compounds of some bivalent metals, e.g. zinc, $[\text{Pt}(\text{CH}_3)_3\text{Cl}]$, CoCl_4^{2-} in Cs_3CoCl_5 , and the optically active arsenic compound:

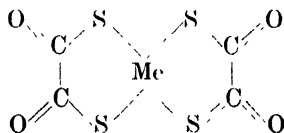


A tetrahedral configuration is found in simple ions XO_4 :



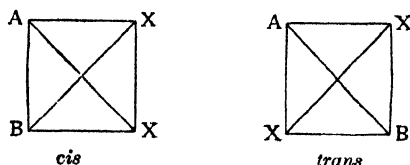
and in many simple covalent compounds of carbon, silicon, etc.

(ii) *Planar arrangement of valencies*. This is found in a number of cases. X-ray examination proves it for the compounds $\text{K}_2[\text{PtCl}_4]$, $\text{K}_2[\text{PdCl}_4]$, $[\text{Pd}^{\text{II}}\text{en}_2\text{Cl}_2]$, $[\text{Co py}_2\text{Cl}_2]$, $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pd}^{\text{II}}(\text{NH}_3)_4][\text{Pd}^{\text{II}}\text{Cl}_4]$, $[\text{Pt}^{\text{II}}(\text{NH}_3)_4]\text{Cl}_2 + \text{H}_2\text{O}$, Cu^{II} with acetylacetonone, benzoylacetonone, etc., dithio-oxalates of Ni , Pt^{II} , Pd^{II} :



When four groups, two of which, X, are identical, are arranged about an atom in a plane square, two geometrical isomers are possible, a *cis*-

isomer when the X-groups are adjacent, and a *trans*-isomer when they are opposite :

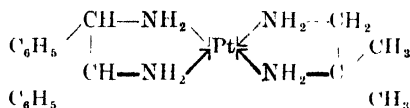


The isolation of *cis-trans* isomers proves the planar arrangement in the glyoximes (p. 419) $[\text{Pd}(\text{NO}_2)_2(\text{NH}_3)_2]$ and Pt^{II} and Pd^{II} compounds with glycine :



The magnetic susceptibility confirms the plane configuration with Pd compounds.

The plane arrangement of valencies was established for bivalent (4-covalent) platinum and palladium by optical activity. In the diphenyl-dimethyl compounds the molecule is dissymmetric and optically active (as was found) when the platinum valencies are in one plane, as shown (the plane of the rings is at right angles to the plane of the paper, the thick lines being above this plane) (Mills and Quibell, 1935) :



With a tetrahedral arrangement of valencies the molecule would have a plane of symmetry and would not be optically active.

(b) *Coordination number 6.* Nuclei of the type $[\text{MeR}_4\text{X}_2]$ can exist in two forms, which are represented by placing the metal atom (Me) at the centre of a regular octahedron with six covalencies directed to the

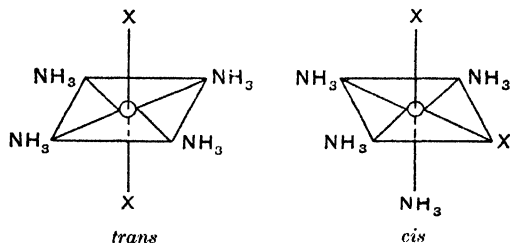
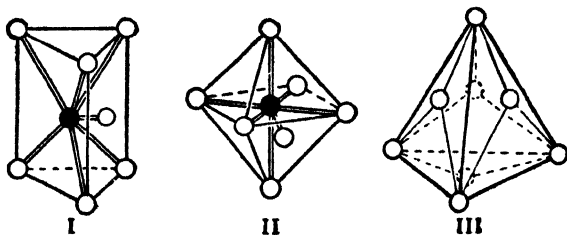


FIG. 243.—*Cis-trans* isomerism in octahedral configuration.

six corners (Fig. 243). (The possibility that the atoms are arranged in a plane hexagon is excluded because this would lead to *three* possible

isomers, whereas only two are known.) The two (univalent) nuclei of the compounds $[\text{Co}(\text{NH}_3)_4\text{X}_2]\text{X}$ are of this type. The *cis*-modifications are distinguished from the *trans*-modifications by their capacity for ring-formation between adjacent groups.

In compounds with coordination number 7, the bonds may be directed either towards the corners of a triangular prism and the centre of one face (I), as in the ion NbF_7''' , or else towards the corners of an octahedron



and the centre of one face (II), as in the ions ZrF_7''' and NbOF_6''' . In the ion $\text{Mo}(\text{CN})_8'''$ in the compound $\text{K}_3\text{Mo}(\text{CN})_8$, in which molybdenum has the coordination number 8, the bonds are directed towards the eight apices of a figure formed by erecting a low regular pyramid on each face of a regular tetrahedron, the whole having twelve triangular faces (III) (the cube form does not occur).

(7) *Optical isomerism.* A convincing argument in favour of Werner's theory is the existence of *optical isomers*. These arise when two compounds have such arrangements of the atoms or groups in space about the central atom that one structure is the mirror-image of the other (*enantiomorphism*). The compounds shown in Fig. 244 are two optically active *cis*-forms (the metal atom is in the centre of the square), and there is also one optically inactive *trans*-form, shown on the right. The bivalent ethylenediamine group *en* in the *cis*-forms engages *two* valencies of the metal atom, one axial and one in the plane.

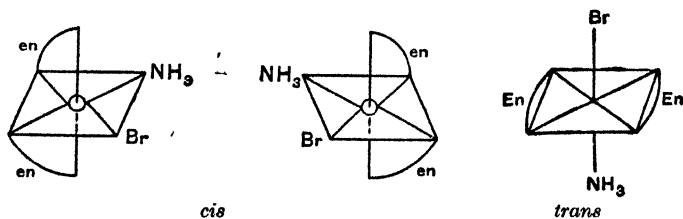


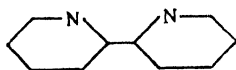
FIG. 244.—Optical activity due to enantiomorphism in octahedral *cis*-configuration.

Instead of ethylenediamine many other 2-coordinating groups can give rise to optical isomerism, *e.g.* the oxalate radical $\text{C}_2\text{O}_4''$ in the

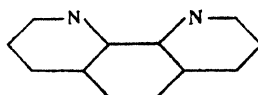
ferrioxalates (Thomas, 1921), $K_3[Fe(C_2O_4)_3]$, and similar compounds with trivalent Al, Cr, Co, Ru, Rh, Ir :



also $\alpha\alpha'$ -dipyridyl (I), α -phenanthroline (II), etc.,



I



II

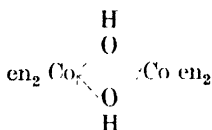
The dipyriddy compounds with bivalent Cu, Fe, Ni, Pt and Ru are resolvable into optical isomers.

An interesting case of high optical activity in a compound free from carbon (Werner, 1914) is that in which the univalent *positive* group containing trivalent cobalt $(HO)_2Co(NH_3)_4$ is coordinated with trivalent cobalt in the compound :

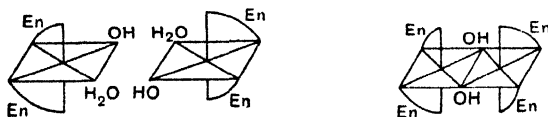


Cases in which the positive charge of a nucleus is raised by the introduction of a positive ion are very rare : usually an increased positive charge arises from expulsion of negative ions by neutral groups.

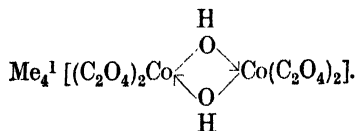
In some cases a nucleus can contain two (or more) central atoms, as in the compound :



formed by loss of water from two molecules :

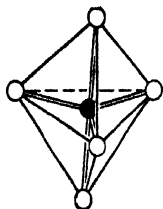


and in the cobaltioxalates (Percival and Wardlaw, 1929) :



Other coordination numbers.—The coordination number 2 is found in some amines, e.g. $[Ni(NH_3)_2]Cl_2$, the number 3 in $K[HgI_3]$.

Examples of the number 5 in coordination complexes are rare, and $\text{Cs}_3[\text{CoCl}_5]$ crystals contain the ions Cs^+ , CoCl_4^{2-} and Cl^- , but there are neutral molecules in which five atoms or groups surround a central atom, *e.g.* PF_5 and $\text{Fe}(\text{CO})_5$. In these the bonds from the central atom are directed to the five corners of a trigonal bipyramid, formed by putting two tetrahedra in contact at a face, as shown in the figure. Coordination compounds in this



class are those containing tervalent nickel and triethylphosphine, $[\text{NiBr}_3(\text{PEt}_3)_2]$ and $[\text{NiCl}_3(\text{PEt}_3)_2]$ ($\text{Et} = \text{C}_2\text{H}_5$), which are formed by oxidising the compounds of bivalent nickel containing NiBr_2 and NiCl_2 with bromine and chlorine, respectively. Similar compounds with cobalt are known.

CHAPTER XXV

THE THEORY OF VALENCY AND THE STRUCTURE OF MOLECULES

The Bohr atom model. --The simplest atom, that of hydrogen (At. No. 1), consists according to Bohr (1913) of one electron of charge $-e$ rotating around a nucleus of charge $+e$, *i.e.* a proton. First consider the orbits to be circles. If the nucleus were the sun and the electron a planet subject to gravitational forces, *any* orbit would be possible, each with an appropriate kinetic energy of the planet which would keep it in that orbit against the pull of gravitation tending to drag it into the sun. In the case of the proton and electron this is not possible, since the moving electron would give out radiation, gradually lose energy, and fall spirally into the nucleus. Bohr assumed that there is now a limited number of *stationary orbits*, in each of which the electron rotates without radiation, whilst when it passes from one orbit to another it emits radiation according to the quantum equation :

$$E_1 - E_2 = h\nu$$

where E_1 and E_2 are the energies in the initial and final orbits, h is Planck's constant (p. 347), and ν the frequency of the emitted radiation. The difference between the energies of the electron in the two orbits is emitted as the energy quantum $h\nu$.

An electron starting at an infinite distance will pass into successive orbits each nearer the nucleus, giving off energy between each transition until it arrives at the smallest possible orbit (nearest the nucleus), when the atom is said to be in the *normal state*.

The possible orbits form a series of circles with the nucleus at the centre. Each orbit is characterised by a quantum number n , which determines the energy of the electron according to, and is itself defined by, the equation :

$$E_n = -K\hbar/n^2, \dots\dots\dots(1)$$

where K is a constant, having for the hydrogen atom the value :

$$K = 2\pi^2e^4m/\hbar^3 = 3.29 \times 10^{15}, \dots\dots\dots(2)$$

e and m being the charge and mass of the electron, and h Planck's constant. In passing from an orbit of quantum number n_1 to one of quantum number n_2 , the energy radiated is :

$$E_1 - E_2 = \Delta E = K\hbar \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right), \dots\dots\dots(3)$$

and hence by the quantum equation, the frequency of the light emitted will be :

$$\nu = \Delta E/h = K \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \dots \dots \dots (4)$$

It is important to notice that ν is *not* the frequency of revolution of the electron in its orbit.

When n_2 is given a small whole number value, 1, 2, 3 ; and n_1 given a series of higher whole number values (*e.g.* $n_2 = 2$; $n_1 = 3, 4, 5, \dots \infty$), equation (4) gives with great accuracy the frequencies (or wavelengths $\lambda = c/\nu$, where $c =$ velocity of light) of the lines in the various spectral series of hydrogen (*e.g.* with the values just quoted the various lines of the **Balmer series**, four of which were mentioned on p. 166). Thus n is always a whole number (zero excluded) from 1 to infinity. K/n^2 is called a **term**.

If the nucleus has a charge $+Ze$, and there is still a single electron of charge $-e$ rotating about it, the value of K in (4) is replaced by Z^2K , *e.g.* for the singly ionised helium atom ($Z = 2$), the spectra are given by equation (4) with $4K$ instead of K . This is true only when there is a single outer electron, since otherwise the electrons surrounding the nucleus exert a screening effect on its positive charge.

The quantum numbers.—Still confining our attention to the hydrogen atom, we may recall that the actual orbit of a planet round the sun, according to Kepler's laws, is an ellipse with the sun at a focus rather than a circle, and as well as circular electronic orbits we may also have

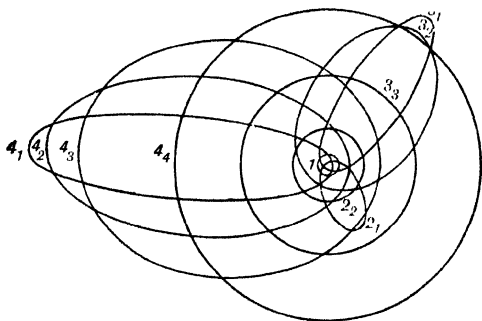


FIG. 245. --Bohr orbits.

elliptical orbits in which the electron has the same energy as in a corresponding circular orbit. Each orbit will thus, by (1), be characterised by a **total quantum number** n , but each ellipse for a given value of n requires another number k for its definition, called a **subsidiary quantum number** : k has also whole number values (zero excluded). Very nearly, the ratio of the total to the subsidiary

quantum number n/k is that of the major to the minor axis of the ellipse. For the circular orbit this ratio is 1, and the orbit for which the principal and subsidiary quantum numbers are equal ($n = k$) is always a circle.

If we denote a particular orbit for which the two quantum numbers are n and k by n_k , the orbit n_n is always a circle. For a total quantum number n , the quantum number k may have n values, *viz.* 1, 2, 3, ... n . For a principal quantum number 4 ($n = 4$), $k = 1, 2, 3, 4$, and the four possible orbits are one circle 4_1 , and three ellipses $4_2, 4_3$ and 4_4 , in which the ratios of the major to the minor axes are 4 : 1, 4 : 2 and 4 : 3, respectively. These orbits are shown in Fig. 245 together with the $1_1 ; 2_1, 2_2 ;$ and $3_1, 3_2, 3_3$ orbits.

The splitting of spectrum lines when the source (*e.g.* a sodium flame) is in a magnetic field (**Zeeman effect**) introduces a third or **magnetic quantum number** m , which defines the angle between the plane of the electron orbit and the direction of the magnetic field.

Additional refinements appear in spectra as **fine structure**: each hydrogen line, previously regarded as single, really consists of two, very close together, but visible with spectroscopic apparatus of high resolving power. To explain this requires a fourth quantum number, which defines the *spin* of the electron about its own axis; this gives the electron a moment of momentum and also a magnetic moment (since it acts as a circular current). Each of these always has the same numerical value but the spin may be in one of two directions, so that this **spin quantum number** s can have two values only, which are $+\frac{1}{2}$ and $-\frac{1}{2}$.

In place of Bohr's k , the new quantum theory introduces a quantum number $l = k - 1$, always 1 less than k . Every electron in the atom is now characterised by definite values of *four* quantum numbers:

$$\begin{aligned} n &= 1, 2, 3, \dots \infty \\ l &= 0, 1, 2, \dots (n - 1); \\ m &= l, (l - 1), (l - 2), \dots 1, 0, -1, \dots (-l + 1), -l; \\ s &= +\frac{1}{2}, -\frac{1}{2}. \end{aligned}$$

The spin and the revolution of the electron in its orbit combine to give different values of an **inner quantum number** j , and for an atom with one electron:

$$j = l \pm s = l \pm \frac{1}{2}.$$

For the smallest value of l , viz. 0, j is given only one value, $+\frac{1}{2}$, but for all higher values of l it has two values, corresponding with the doublet character of the spectral terms.

It will be seen that the magnetic quantum number m as here defined has all positive and negative values of l , including zero, and for each value of l there are $(2l + 1)$ values of m .

Pauli's principle.—In an atom containing more than one electron an empirical rule called **Pauli's principle** holds: *in the same atom there cannot be more than one electron having all four quantum numbers, n, l, m , and s the same.* Thus, there can be only two electrons having the same values of n, l , and m , and for one of these $s = +\frac{1}{2}$ and for the other $s = -\frac{1}{2}$.

If $n = 1$, then $l = 0$ and $m = 0$. There are two values of s , $+\frac{1}{2}$ and $-\frac{1}{2}$, hence there can be only *two* electrons of principal quantum number $n = 1$.

If $n = 2$, then $l = 0$ or 1. For $l = 0$, $m = 0$ and $s = \pm\frac{1}{2}$. For $l = 1$, m has the possible values 1, 0, -1. Each of these can be associated with two values of s , $\pm\frac{1}{2}$, giving six possible cases, and with the two for $l = 0$ eight in all.

If $n = 3$, l can be 0, 1 and 2, and the values of m for the three cases are 0, (1, 0, -1), and (2, 1, 0, -1, -2), respectively, or 9 in all. Each can have the two values of s , $\pm\frac{1}{2}$, making a total of 18.

If $n = 4$, l can be 0, 1, 2, and 3, and the values of m for the four cases are 0, (1, 0, -1), (2, 1, 0, -1, -2) and (3, 2, 1, 0, -1, -2, -3),

respectively, or 16 in all. Each of these can have the two values of s , $\pm \frac{1}{2}$, making a total of 32.

Since the maximum number of values of m is $(2l + 1)$ and each can be associated with the two values of s , $\pm \frac{1}{2}$, the maximum number of electrons in a sub-group is $2(2l + 1)$:

TABLE I

Level n_l -	- 1 ₀	2 ₀ 2 ₁	3 ₀ 3 ₁ 3 ₂	4 ₀ 4 ₁ 4 ₂ 4 ₃
l -	- 0	0 1	0 1 2	0 1 2 3
Max. no. of electrons -	2	2 6	2 6 10	2 6 10 14
	2	<u>8</u>	<u>18</u>	<u>32</u>

In spectrum notation letters are used to denote the values of the quantum number l :

l -	- 0	1	2	3	4	5
Symbol -	s	p	d	f	g	h

Thus a $3p$ electron has $n = 3$ and $l = 1$. (The symbol s is also used for the spin quantum number, and the two uses must not be confused.) An upper index denotes the number of electrons in the given state: thus $1s^2 2p^4$ (read "two in $1s$," etc.) means two electrons with $n = 1$ and $l = 0$, and four electrons with $n = 2$ and $l = 1$.

The Periodic table.— Since the numbers of electrons in the groups in Table I correspond with the numbers of elements in the periods of the periodic table:

2	8	8	18	18	32	[10]
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it was at first thought that, as each period (except the last incomplete period) ends with an inert gas:

He	Ne	Ar	Kr	Xe	Rn	—
----	----	----	----	----	----	---

the numbers should give the numbers of electrons in the outer electron shells of the inert gases. It is now known that *the outer electron group is 8 for all the inert gases*, and hence after argon some of the inner shells of electrons must be left incomplete whilst an s -electron shell builds up over them. The successive electron shells, starting with the one nearest the nucleus, are symbolised in X-ray notation (p. 393) as K , L , M , N , O , P and Q .

The group of 2 electrons with $n = 1$ completed with helium forms a K -shell nearest the nucleus which is also present in the atoms of all the other elements. Above this, a shell of from 1 to 8 electrons is completed from lithium to neon, the nuclear charge increasing in steps of 1, and the mass by larger steps by addition of both protons and neutrons to the nucleus. These 8 electrons with $n = 2$ complete a second or L -shell. A third or M -shell of 8 electrons with $n = 3$ is formed on passing from sodium to argon.

The electrons in each group with the same principal quantum number n are not all equivalent, since they have different values of the serial quantum number l , as required by Pauli's principle. In lithium there is one $2s$ electron ($n = 2$, $l = 0$), in beryllium two, and this is the maximum number. They are valency electrons. Of the three $n = 2$

electrons in boron there are two $2s$ and the third must be a $2p$ ($n=2$, $l=1$) electron. There can be six $2p$ electrons, and this maximum is reached with neon. Fluorine and oxygen atoms tend to bind these electrons to reach a stable neon structure, but as their nuclear charges are only 7 and 6, respectively, they then form the negative ions F^- and O^{--} , neon with a nuclear charge of 8 being neutral with 8 outer electrons.

In the next period $n=3$ and the electrons form an M -shell. Sodium has one $3s$ electron, magnesium two, and this is the maximum number for $n=3$, $l=0$. In aluminium the third electron is a $3p$ ($n=3$, $l=1$), and the six $3p$ electrons possible are added when argon is reached.

The next period is a long period of 18 elements. In potassium the first electron goes into a $4s$ ($n=4$, $l=0$) level, and ten $3d$ ($n=3$, $l=2$) levels are left empty for the time, since the energy in a $4s$ level is smaller than that in a $3d$ level, and the electron occupies a level in which it has a lower energy.

Calcium has two $4s$ valency electrons. With scandium, owing to the increased nuclear charge, the inner level begins to fill and the electron goes into the $3d$ level. The outer structure of argon, $2 | 2 6 | 2 6 |$, has begun to fill up towards its maximum of 18, and the scandium structure is $2 | 2 6 | 2 6 1 | 2$, derived from that of calcium $2 | 2 6 | 2 6 | 2$ by addition of an electron to an inner $3d$ level. This goes on as far as chromium, when one of the two outer $4s$ electrons drops to a $3d$ level, which now contains 5 electrons. These remain in manganese and the next electron goes into the $4s$ level (see Table II, p. 432).

Iron, cobalt and nickel have 6, 7 and 8 electrons, respectively, in $3d$ levels. With copper, another electron drops from the $4s$ level, making $8 + 10 = 18$ in the $3s$, $3p$ and $3d$ levels and 1 in the outer $4s$ level. The inner 3-quantum levels now contain the maximum number of 18 electrons allowed by Pauli's principle (Table I). This completed inner group of 18 electrons persists unchanged in all the remaining elements.

The arrangement of electrons in the elements from titanium to copper is required by the spectra and also explains (i) the chemical and physical properties of the elements V, Cr, Mn, Fe, Co and Ni, viz. the arrest of the valency to 2 or its variation by *one* unit at a time (although V, Cr and Mn have very varying valencies, as shown below, these differ by one), (ii) the paramagnetism and (iii) the colour of the ions (supposed to be characteristic of incomplete inner groups), (iv) the changes of direction in the X-ray curves (Fig. 231), and (v) the appearance of the first triad (Fe, Co, Ni).

Element.	Valencies.				
Ti	2	3	4		
V	2	3	4	5	
Cr	2	3		6	
Mn (1)	2	3	4	6	7
Fe (1)	2	3		6	
Co (1)	2	3			
Ni (1)	2	3	4		
Cu	1	2			

This filling up of *incomplete* inner levels was first suggested by Ladenburg (1920) and explained by Bohr.

TABLE II

n=	l=	K		L		M		N		O		P		n=	l=	K	L	M	N	C		P		Q
		s	p	s	p	s	p	s	p	s	p	s	p							s	p	s	p	
1	H He	1	2													1	2							7
2	Li Be	2	2													2	2							8
3	B C	2	2	1	2											2	2							9
4	N O	2	2	1	2	1	2									2	2							10
5	F Ne	2	2	1	2	1	2	1	2							2	2							11
6	Na Mg	2	2	1	2	1	2	1	2							2	2							12
7	Al Si	2	2	1	2	1	2	1	2							2	2							13
8	P S	2	2	1	2	1	2	1	2							2	2							14
9	Cl Ar	2	2	1	2	1	2	1	2							2	2							15
10	K Ca	2	2	1	2	1	2	1	2							2	2							16
11	Sc Ti	2	2	1	2	1	2	1	2							2	2							17
12	V Cr	2	2	1	2	1	2	1	2							2	2							18
13	Mn Fe	2	2	1	2	1	2	1	2							2	2							19
14	Co Ni	2	2	1	2	1	2	1	2							2	2							20
15	Cu Zn	2	2	1	2	1	2	1	2							2	2							21
16	Ga Ge	2	2	1	2	1	2	1	2							2	2							22
17	As Se	2	2	1	2	1	2	1	2							2	2							23
18	Br Kr	2	2	1	2	1	2	1	2							2	2							24
19	Rb Sr	2	2	1	2	1	2	1	2							2	2							25
20	Y Zr	2	2	1	2	1	2	1	2							2	2							26
21	Nb Mo	2	2	1	2	1	2	1	2							2	2							27
22	Pd Ag	2	2	1	2	1	2	1	2							2	2							28
23	Cd In	2	2	1	2	1	2	1	2							2	2							29
24	Sn Sb	2	2	1	2	1	2	1	2							2	2							30
25	Te I	2	2	1	2	1	2	1	2							2	2							31
26	Ba La	2	2	1	2	1	2	1	2							2	2							32
27	Ce Pr	2	2	1	2	1	2	1	2							2	2							33
28	Nd Pm	2	2	1	2	1	2	1	2							2	2							34
29	Sm Eu	2	2	1	2	1	2	1	2							2	2							35
30	Gd Tb	2	2	1	2	1	2	1	2							2	2							36
31	Dy Ho	2	2	1	2	1	2	1	2							2	2							37
32	Er Tm	2	2	1	2	1	2	1	2							2	2							38
33	Yb Lu	2	2	1	2	1	2	1	2							2	2							39
34	Hf Ta	2	2	1	2	1	2	1	2							2	2							40
35	Ta W	2	2	1	2	1	2	1	2							2	2							41
36	Re Os	2	2	1	2	1	2	1	2							2	2							42
37	Ir Pt	2	2	1	2	1	2	1	2							2	2							43
38	Au Hg	2	2	1	2	1	2	1	2							2	2							44
39	Tl Pb	2	2	1	2	1	2	1	2							2	2							45
40	Bi Po	2	2	1	2	1	2	1	2							2	2							46
41	At Rn	2	2	1	2	1	2	1	2							2	2							47
42	Fr Ra	2	2	1	2	1	2	1	2							2	2							48
43	Ac Th	2	2	1	2	1	2	1	2							2	2							49
44	Pa U	2	2	1	2	1	2	1	2							2	2							50
45	Np Pu	2	2	1	2	1	2	1	2							2	2							51
46	Am Cm	2	2	1	2	1	2	1	2							2	2							52
47	Bk Cf	2	2	1	2	1	2	1	2							2	2							53
48	Es Fm	2	2	1	2	1	2	1	2							2	2							54
49	Md No	2	2	1	2	1	2	1	2							2	2							55
50	Lr	2	2	1	2	1	2	1	2							2	2							56

From copper to krypton the $4s$ and $4p$ levels fill up normally until with krypton they contain $2 + 6 = 8$ electrons and the period is complete.

A new period begins with rubidium, in which a loosely-bound $5s$ electron appears, the $4d$ and $4f$ levels remaining empty. After strontium, with two $5s$ electrons, the next electron goes into a lower $4d$ level in yttrium, and this level is gradually filled, reaching ten electrons in palladium, in which the $5s$ electron drops back into a $4d$ level. The $5s$ and $5p$ levels fill up normally to a complete $2 + 6 = 8$ group with xenon, which closes the period. In copper all the inner levels (including the $3d$) are filled, but in silver the $4f$ levels are empty.

In the period beginning with caesium a $6s$ electron is added, in barium two $6s$ electrons. From and including lanthanum, however, the valencies remain constant at 3 until the last rare-earth element lutecium is reached, all the electrons going to complete the empty $4f$ levels deep inside the atom. To the eighteen electrons of levels of principal quantum number 4 there are now added in succession fourteen more, making up a total of 32, the maximum possible for $n = 4$. Since all are well within the stable octet completed in xenon they have no appreciable influence on the chemical properties, which remain practically constant, and this explains both the number (15) and chemical properties of the rare-earth elements in this period (sometimes called *lanthanides*, to distinguish them from the total number of rare-earth elements which includes scandium and yttrium in earlier periods). Just as in the fourth and fifth periods, the arrangement of electrons in the rare-earth elements is accompanied by the appearance of coloured ions and paramagnetism.

The element following lutecium cannot be a rare-earth element but must be a fourth group element related to zirconium. This was confirmed by the properties of hafnium, discovered by Coster and Hevesy.

In the following elements as far as gold, the $5s$ and $5p$ levels of xenon, containing 8 electrons, are completed by the addition of ten electrons to the $5d$ levels, making a total of 18, whilst in gold the $n = 6$ levels begin to fill, leading to the completion of the $6s$ levels with $2 + 6 = 8$ electrons, forming the outer shell of the inert emanation. In the remaining fragmentary period, the $7s$ level begins to be occupied. The $6d$ level begins to fill with actinium. Elements 93 to 96 are artificial transuranic elements (p. 407) and are supposed to be transitional elements of Group III like the earlier lanthanides in this group. It has been suggested that these transitional elements begin with actinium, hence they are called *actinides*. The alternative configurations are shown at the foot of Table II.

It is seen that each period is characterised by a principal quantum number n , equal to the number of the period. The electrons in the atoms are arranged in groups or shells, each fully occupied when it contains $2n^2$ (2, 8, 18, 32) electrons, and these groups are divided into sub-groups defined by the serial quantum number l , the number (2, 6, 10, or 14 for $l = 0, 1, 2,$ or 3) in each complete sub-group being $2(2l + 1)$. This arrangement was introduced by Bury (1921) on chemical grounds, and by Stoner (1924) from spectroscopic results, and it is required by Pauli's principle.

Valency.—Heitler and London (1927) pointed out that the two shared electrons forming a covalent bond (electron-pair bond) in Lewis's theory (p. 412) have opposite spins, $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$, and as each electron may pair with another of opposite spin the valency of an atom is equal to the number of unpaired electrons in the valency shell. The resultant spin $S = \sum s$ gives the spin due to unpaired electrons, each contributing $\frac{1}{2}$ unit, hence the valency is

$$V = 2S = \text{number of unpaired electrons.}$$

Each valency bond formed from two unpaired electrons, one in each uniting atom, reduces S by unity, hence V decreases in multiples of 2,

TABLE III. VARIABLE VALENCIES

Group.	Element					Valencies			
	$n=2$	3	4	5	6	1	+3	+5	+7
VII	(F)	Cl	Br	I	—	1	+3	+5	+7
VI	(O)	S	Se	Te	(Po)	2	2	4	6
V	N	P	As	Sb	Bi			3	5
IV	C	Si	Ge	Sn	Pb			2	4
III	(B)	(Al)	(Ga)	In.	Tl			1	3

as is commonly found (see Table III: + denotes loss or sharing of electrons, - gain of electrons).

TABLE IV. COVALENCIES

n	1			2			n	1			2			3						
l	0	0	1				l	0	0	1	0	0	1	0	1	0	1	0	1	2
m	0	0	-1 0 1				m	0	0	-1 0 1	0	0	-1 0 1	0	-1 0 1	-2	-1 0 1 2			
H	1						P	2	2	2 2 2	2	2	2 2 2	2	1 1 1					
He	2							2	2	2 2 2	1	1	1 1 1	1						
Li	2	1					S	2	2	2 2 2	2	2	2 1 1							
Ber	2	1	1					2	2	2 2 2	2	2	1 1 1	1						
B	2	2	1					2	2	2 2 2	1	1	1 1 1	1 1						
	2	1	1 1																	
C	2	2	1 1				Cl	2	2	2 2 2	2	2	2 2 1							
	2	1	1 1 1																	
N	2	2	1 1 1					2	2	2 2 2	2	2	2 1 1	1						
O	2	2	2 1 1					2	2	2 2 2	2	2	1 1 1	1 1						
F	2	2	2 2 1					2	2	2 2 2	1	1	1 1 1	1 1 1						

Table IV gives results for twelve elements of the first periods. The figures in the table give the numbers of electrons with the stated quantum numbers, and the valency V is equal to the number of unpaired electrons (which can pair with electrons of opposite spins of other atoms), *i.e.* the sum of the values of 1 in the table, values of 2 denoting paired electrons. Bivalent and quadrivalent carbon are both possible; nitrogen has a covalency of 3 only, fluorine only of 1, and oxygen only of 2, whilst phosphorus can have valencies of 3 and 5, sulphur of 2, 4, and 6, and chlorine of 1, 3, 5, and 7.

Wave Mechanics. The details of Bohr's theory, which postulate electrons as point charges revolving in orbits around the nucleus, have been abandoned for reasons which need not be stated. The explanation of the structure of the periodic table on pp. 430-433 is still valid, as it depends only on Pauli's principle and on energy levels of electrons which are spectroscopic data.

The modern theory of atomic structure is based on *the wave nature of the electron*. Electrons in motion behave as if they were associated with waves, the lengths of which are given by de Broglie's formula (1924):

$$\lambda = h/mv$$

where h is Planck's constant, and m and v the mass and velocity of the electron, so that mv is its momentum.

Beams of electrons are diffracted by matter, *e.g.* by reflexion from a crystal or by passage through thin metal foil, in the same way as X-rays. This dual aspect of an electron is like the dual character of light, which sometimes behaves as if it consists of corpuscles or photons (*e.g.* in the photoelectric effect, when electrons are expelled from metals by ultra-violet light) and sometimes as waves, which give rise to interference and diffraction.

Schrodinger (1926) supposed that the charge of an electron is not concentrated in a particle but extends in space as a "cloud", the density of which at any point is proportional to ψ^2 , where ψ is a *wave function*. Born (1926) retained the idea of the electron as a particle and supposed that ψ^2 gives the probability of its occurrence in any given part of space. An equation connecting ψ and E , the energy of the electron, has satisfactory solutions only for a set of definite values of E . For the electron in a hydrogen atom these values of E are the same as those given by Bohr's equations (1) and (2), p. 427, without any special assumption of non-radiating orbits, the orbits being now replaced by the wave function ψ .

Theory of directed bonds.— This theory gives an explanation of directed covalent bonds. The wave function of an s -electron ($l = 0$) is a sphere. The p -electrons ($l = 1$) have wave functions denoted by p_x , p_y , and p_z at right angles, and these give rise to directed bonds. A bond is formed by the overlapping of regions in which the wave functions ψ (or the electron charge densities, proportional to ψ^2) have pronounced values.

The s -electron of a hydrogen atom may be represented by a sphere (since its wave function has spherical symmetry) and the combination of two hydrogen atoms by overlapping spheres. The bond strength for an s -electron is taken as unity.

Oxygen has four p -electrons ($l=1$) which are in different states, according to a *rule of maximum multiplicity* which says that when electrons are added successively as many levels ("orbits") are singly occupied as possible before any pairing of electron spins occurs. There are three p -orbitals with wave functions p_x, p_y, p_z directed along three axes x, y, z at right angles, and the electron densities are dumb-bell shaped (Fig. 246) when the orbitals are occupied by electrons. The bond strength is represented by $\sqrt{3}$. Of the four p -electrons, two go singly into two orbitals according to the rule, but the other two electrons are forced to go together, with anti-parallel (opposite) spins, into the remaining orbit. Thus, two unpaired valency electrons are available to combine with two s -electrons of opposite spins of two hydrogen atoms to form H_2O .

Another rule states that a bond is formed by the maximum overlapping of wave functions. Hence the hydrogen atoms must approach

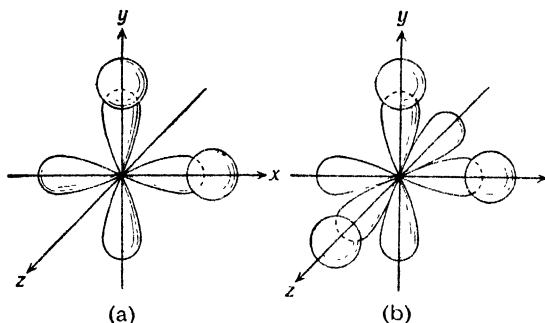


FIG. 246.— Formation of directed bonds.

along the two directions of the axes of the wave functions of the two valency p -electrons of the oxygen, which are at right angles, and the H_2O molecule formed is shown in Fig. 246a. Owing to repulsion of the two hydrogens the angle is greater than 90° , probably 106° , but in H_2S the angle is practically 90° . This type of binding is called sp^2s .

Nitrogen has three p -electrons and these can occupy singly the p_x, p_y and p_z orbitals, and combine with the s -electrons of three hydrogen atoms, forming a molecule NH_3 with the three bonds at right angles, and with p^3s^3 binding (Fig. 246b).

Hybridisation.—The normal carbon atom $1s^2 2s^2 2p^2$ has only *two* p -electrons, and we might expect a compound CH_2 , since the spins would be unpaired and would combine with anti-parallel spins of two s -electrons, one in each hydrogen atom. To exert four valencies *one* of the $2s$ -electrons ($n=2, l=0$) must be excited and pass from its normal $2s$ -state to a $2p$ -state, when the atom becomes $1s^2 2s^1 2p^3$ with *four* unpaired spins. The directions of these valencies might be supposed to be one undirected, and three at right angles (p_x, p_y and p_z) as in nitrogen. When, however, the bond energy greatly exceeds the excitation energy for raising an electron from an s - to a p -level, the quantisation changes and s - and p -electrons assume equivalent wave functions of strength 2 directed towards the four corners of a regular tetrahedron, so that CH_4 is formed as a tetrahedral

molecule. This process is called *s-p-hybridisation*, since the actual wave functions of the bonds are formed by combining *s*- and *p*-functions to form stronger bonds than either separately.

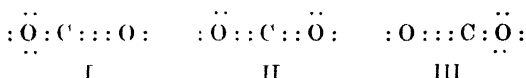
The nitrogen in NH_4^+ has one *s*- and three *p*-electrons, so that conditions for hybridisation occur and the ammonium ion is tetrahedral.

Resonance.—The name *resonance* was given by Pauling (1933) to a state in which the electron configuration of a molecule can be represented in two or more ways, subject to the conditions that: (i) the positions of the atoms remain approximately unchanged, (ii) the energies of the various states are not very different, and (iii) the structures have the same number (including zero) of unpaired electrons.

The energy of a molecule is lower when it is in a state comprising the various possible separate electronic configurations at the same time than the energy for any one of the latter. Since a molecule is more stable the less its energy content, the existence of resonance will correspond with increased stability.

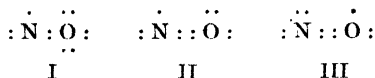
The actual resonance state is not a mixture of molecules each in one of the separate states, but is a single state comprising all the possible states to some extent. Where resonance, due to electron transfer, is between a single and double bond, the actual bond is intermediate and has some single bond and some double bond character. As a rough analogy it may be said that if two possible states of a molecule could be coloured red and blue, the actual state is not a mixture of red and blue molecules, but all purple molecules, the red or blue shade of purple depending on the proportion of these forms in the resonance hybrid.

The formula of carbon dioxide could be written as

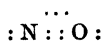


and for each the O to O distance should be about 2.44 Å. and the heat of formation from the atoms about 350 k.cal. per gm. mol. The observed values are 2.32 Å. and 380 k. cal. The shortened bond distance and the smaller energy of the molecule (380–350 = 30 k. cal.) suggest that the molecule is a resonance hybrid. Forms I and III involve electron transfer and would give the molecules an electric moment (p. 440). Since II has no moment, if I and III are involved they must contribute by equal amounts. It will be noticed that I and III are different forms, since the molecule is not supposed to have time to rotate during the electronic transfer.

Nitric oxide may be represented as a resonance hybrid of

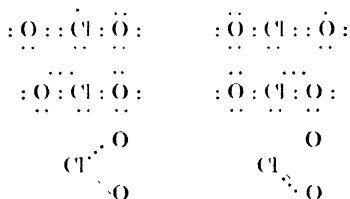


and since the gas has a small electric moment, forms I and III do not contribute equally. This case, where an odd electron appears, is regarded by Pauling as an example of a *three-electron bond*, i.e. resonance between $\text{A}::\text{B}$ and $\text{A}::\dot{\text{B}}$, and represented by

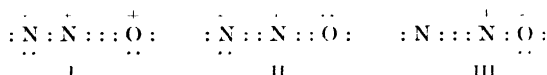


and the oxygen molecule (which is paramagnetic and hence cannot have completely paired electrons as in $\ddot{\text{O}}::\ddot{\text{O}}$) has two three-electron bonds $:\ddot{\text{O}}:\ddot{\text{O}}:$, corresponding with $:\ddot{\text{O}}:\ddot{\text{O}}:$ with two unpaired electrons.

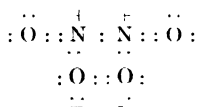
Another example of a molecule containing an odd electron and perhaps a three-electron bond is chlorine dioxide (p. 277), which is bent and probably is a resonance hybrid of the forms :



The adjacent charge rule (Pauling, 1932) states that structures in which adjacent atoms have the same charge are less important than other structures. Thus, in nitrous oxide N_2O structure I makes no appreciable contribution as compared with structures II and III :



whilst in carbon dioxide all three structures are important. The rule does not agree with the structure usually given to N_2O_4 :



Sizes and Shapes of Molecules. Several methods provide quantitative information about: (i) the distances between the centres of atoms in molecules (or ions in crystal lattices), (ii) the modes of arrangement of these atoms, and (iii) the angles between the valency bonds linking the atoms together. The most important methods are :

1. *Diffraction of X-rays and of electrons* by solids, liquids, and gases.
2. *Spectroscopic methods*, including Raman, infra-red, and visible band spectra.
3. *Electric dipole moments*.
4. *Magnetic susceptibility*.

X-ray methods.—The *X-ray method* as applied to crystals has been described. It has been used to investigate the so-called “amorphous solids” (e.g. glasses), liquids and even gases and vapours. The “powder method” often gives diffraction patterns in these cases, indicating some regularity in molecular arrangement of liquids and of molecular structure in gases. Liquid water and mercury show characteristic spacings, and the structure of water has been deduced from the results.

Glass seems to consist of minute crystals (size 10^{-6} to 10^{-7} cm.) with a random arrangement. Plastic sulphur has a fibrous structure composed of long chains of sulphur atoms. The diffraction of X-rays by gases has been superseded by the electron diffraction method, with which a much shorter exposure is required.

Electron diffraction.—The *electron diffraction method* depends on the wave nature of the electron, beams of which are diffracted like X-rays by matter. This method has shown that the molecules HgCl_2 , HgBr_2 , HgI_2 , C_2N_2 , CS_2 and C_3O_2 are linear; BCl_3 is planar and triangular; SiCl_4 , GeCl_4 , TiCl_4 , $\text{Ni}(\text{CO})_4$ and P_4 are tetrahedral; PF_5 is a trigonal bipyramid; SF_6 is octahedral; PF_3 is pyramidal; and F_2O , Cl_2O and SO_2 are bent at angles of 100° , 115° and 120° , respectively. The interatomic ("bond") distances vary from 1.5 to 2.5 Å.

The bond length is important in deciding the bond character and the presence of resonance. The distances between the centres of atoms joined by covalencies are regulated by the so-called *normal covalency radii* of atoms, the length of the bond being the sum of the valency radii of the two atoms it joins.

Optical methods.—The *infra-red absorption spectra* give information on the moments of inertia and hence the interatomic distances in the case of molecules having electric moments. Isotopic molecules (e.g. H^{35}Cl and H^{37}Cl) have different moments of inertia and hence are detected in band spectra.

More accurate results are obtained by so-called *rotation-vibration spectra*; and absorption spectra in the *visible spectrum*, due to electronic motions, are applicable in the case of molecules without permanent electric moments.

In light scattered from a transparent liquid or solid, extra lines with a small frequency difference appear alongside the line in the spectrum due to the incident monochromatic light. From these *Raman spectra* the vibrational frequencies for the pairs of atoms in the molecule, equal to the frequency differences, are found, and by assuming simple harmonic vibration the restoring forces for unit displacement (measuring the bond strengths) may be calculated. With single, double, and triple bonds the restoring forces are approximately in the ratio 1 : 2 : 3.

The heats of dissociation of molecules given on p. 283 are mostly calculated from the vibrational band spectra of molecules, which consist of groups of lines. When the vibrational energy of the atoms becomes so large that the atoms fly apart their motion is no longer quantised and the lines towards the high-frequency end of the spectrum, which are crowding closer together, pass over into a continuous spectrum. The frequency where the continuum begins gives the energy $h\nu$ required to dissociate the molecule into atoms, and after

correction if one or both atoms are in excited states, the heat of dissociation into normal atoms is found.

Electric dipole moments.—Many covalent molecules possess a *permanent electric dipole*, the strength of which is expressed as the *electric dipole moment* μ .

A dipole moment will be produced by an *unequal sharing*, on the average, of the electrons forming the bond between two atoms. In the HCl molecule, on the average, the valency electrons spend more time near the chlorine nucleus, with its larger positive charge, than near the hydrogen nucleus. The molecule thus behaves as if the chlorine end were negative and the hydrogen end positive, and this may be represented by the symbol $\overset{+}{\text{H}}\overset{-}{\text{Cl}}$, where the point of the arrow shows the negative end and the cross the positive end. The electric moment is a vector quantity (it has magnitude and direction), and it may be calculated by adding the moments of the various atom or radical bonds by vector addition like the parallelogram of forces. In this, suitable bond angles must be assumed to give the correct resultant, and from these angles some idea of the shape of the molecule can be obtained.

Molecules with or without a permanent dipole acquire an *induced dipole* under the influence of an electric field and in the direction of this field. In this case the electron shell of an atom is displaced relative to the positive core and the result is equivalent to the formation of a positive and negative doublet (Fig. 247). This is stronger the more polarisable the atom, molecule, or ion, and the effect (which can be measured from the refractive index) enables ionic radii to be calculated.

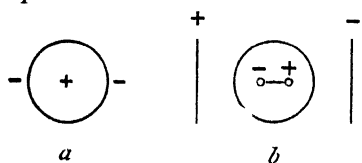


FIG. 247.—Deformation of charges to produce an induced dipole.

The field produced by a charged ion in a crystal may be about 10^8 volts per cm., and thus capable of producing deforming effects on neighbouring ions.

Ions in solution will tend to produce dipoles in the solvent molecules, so that the latter will arrange themselves around the ion with the axes of the dipoles towards the centre of the ion and the charge of the dipole opposite to that of the ion pointing towards it. An ion in water, for example, is surrounded by such a sheath of polarised water molecules, which it drags about with it in the solution (see p. 240).

Molecules containing permanent dipoles are known as **polar molecules** and generally show peculiar properties. When they are liquids they usually: (i) are associated, (ii) have abnormally high boiling points, (iii) have high dielectric constants, (iv) are good ionising solvents. Whereas many properties of mixtures of **non-polar liquids** (such as

benzene and other hydrocarbons) are almost additively composed of those of their constituents, those of mixtures of polar substances (such as water and sulphuric acid) deviate largely from this rule, and in addition there is usually a considerable heat of admixture. As regards the solvent action of the two classes of liquids, it is found that members of each one group are freely miscible with one another but not with members of the other group. With solids, it is found that non-polar substances usually have low melting points unless they have high molecular weights, whilst polar solids such as salts have high melting points. Some non-polar solids such as diamond have high melting points, but are probably atomic lattices. Non-polar solids are often more volatile than salts.

The values of the dipole moments of some molecules, all gaseous except CCl_4 and AgClO_4 which are dissolved in benzene, are given in the table below in electrostatic units $\times 10^{18}$.

N_2 0	HCl 1.034	NH_3 1.49	H_2S 1.1
CO_2 0	HBr 0.788	PH_3 0.55	H_2O 1.8
CCl_4 0	HI 0.382	AsH_3 0.16	AgClO_4 4.7

Distinctively non-polar molecules have zero dipole moment; those in which a shift of electron pairs (covalencies) occurs (HCl, etc.) have a small moment; salts (AgClO_4), and compounds containing semi-polar double bonds, in which electron transfer has occurred, have high moments unless some other compensating effect intervenes.

The effect of the solvent on ionisation of a solute was referred by J. J. Thomson and by Nernst to the dielectric constant. The force between two charges at a distance d in a medium of dielectric constant D is e_1e_2/Dd^2 , so that the attraction tending to bind two ions together is weaker the higher the value of D . Water, hydrocyanic acid and acetonitrile (CH_3CN) are good ionising solvents; the alcohols are medium ionising solvents, and benzene is a poor ionising solvent, as would be expected from the values of D given below:

Water	-	-	-	81	Ethyl alcohol	-	-	26
HCN	-	-	-	116	Sulphur dioxide (liq.)	-	-	13.75
CH_3CN	-	-	-	39	Benzene	-	-	2.29
Methyl alcohol	-	-	-	35				

Mutual deformation of ions.—Optical refraction measurements show that electron shells of anions and water molecules are less deformable when they are close to cations. The action of anions on cations is small, since the cations are usually smaller and less deformable. The deformability of an anion increases with increasing radius and charge; the deforming action of cations increases with increasing charge and decreasing radius.

Some interesting speculations as to the colour of inorganic compounds follow from these considerations. If we consider the salts in the following table, formed from the cations in the vertical row and the anions in the horizontal row, also cations combined with water and

ammonia, the increasing depth of colour in the series fluoride to iodide may be regarded as due to the increasing deformability of the anion, which is increasing in size. Sulphates have the same colour as the fluorides (with a small anion) because the O^{--} ions in SO_4^{--} are relatively fixed owing to the binding forces rendering them less deformable, whilst the oxides themselves, with more deformable O^{--} ions, are much darker in colour. According to Fajans, the blue colour of hydrated cupric salts is (at least in part) due to the deformation of water molecules.

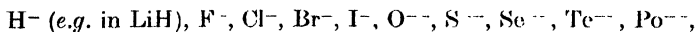
	F	Cl	Br	I	O	S	SO ₄	H ₂ O	NH ₃
Ni ⁺⁺	- Yellowish	Yellow-brown	Dark brown	Black	Dark green	Black	Grey-blue	Green	Blue
Cu ⁺⁺	- White	Yellow-brown	Brown-black	---	Black	Blue-black	White	Blue	Blue
Ag ⁺	- Yellow	White	Yellow-white	Yellow	Dark brown	Black	White	Colourless	Colourless

Fajans pointed out that the tendency to form ionic or covalent links is also related to the deformability of electron shells. Let a positive and negative ion be brought close together. If the deformation of the electron shells becomes so large that there is an actual transfer of electrons, then a covalent link will be formed. This will depend on the attraction exerted by the positive ion on the electrons of the negative ion and on the firmness with which these electrons are held. The attraction of the positive ion increases with its charge and is larger when the ion is small, when the negative ion may approach nearer the charge of the positive ionic core. The ease with which electrons are detached from the negative ion increases with its size, since then the outer electrons, being further from the positive core, are less firmly held. Hence the conditions for the formation of ionic and covalent links may be summarised as follows :

IONIC	COVALENT
Positive charge low.	Positive charge high.
Large cation.	Small cation.
Small anion.	Large anion.

The 18-electron shells are more polarisable than octets and electrons of easily polarisable anions penetrate deeper into them, causing decrease of polarity and stronger binding ; e.g. $HgCl_2$ is much less polar than $CaCl_2$.

The number of negative, as compared with positive, *atomic* ions is small. in solutions and crystals only the following occur :



and they are known only with external configurations of 8 electrons ; those with several valencies do not occur. The reason for the small number is supposed to be related to the tendency of anions with increasing charge to leave the polar state on account of their greater deformability, although the energy changes in the formation of anions and cations are also of importance.

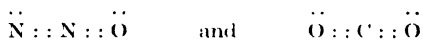
According to V. Goldschmidt (1926) the distances between the atoms in polyatomic ions in crystals depend to an appreciable extent on the nature

of the other ions in the lattice. *E.g.* the distance N—O in the NO_3^- ion is 1.40 A.U. in NaNO_3 and 1.15 A.U. in LiNO_3 , because the small Li^+ ion has a stronger polarising effect on the NO_3^- ion than has the larger Na^+ ion. In a similar way the TiO_3 complex in CaTiO_3 is expanded when Ca^{++} is replaced by the smaller Mg^{++} , and the resulting structure is very similar to AlAlO_3 , the Mg and Ti being approximately equidistant from the nearest oxygen atoms. In some cases a rearrangement of the atoms around the polarising ion may occur, as when the small Be^{++} ion replaces Ca^{++} in spinel, CaAl_2O_4 , when the ions Ca^{++} and $[\text{Al}_2\text{O}_4]^-$ are converted into $[\text{BeO}_4]^{6-}$ and 2Al^{3+} . It is even suggested, on the basis of X-ray results, that ammonium fluoride crystals do not, like other ammonium salts, consist of NH_4^+ and X^- [X^- = halogen ion] but of $\text{NH}_3 + \text{HF}$, owing to the deforming action of the small F^- ion on the NH_4^+ ion.

Magnetism.—As a general rule, molecules containing only pairs of electrons with anti-parallel spins are diamagnetic, whilst molecules and free radicals containing unpaired electrons are paramagnetic. In most cases the magnetism in crystals or in solutions is almost entirely due to the electron spin, that due to orbital motion being eliminated. The

molecules $\text{:}\ddot{\text{N}}\text{:}\text{:}\ddot{\text{O}}\text{:}$ (nitric oxide), $\text{:}\ddot{\text{O}}\text{:}\text{:}\ddot{\text{N}}\text{:}\text{:}\ddot{\text{O}}\text{:}$ (nitrogen dioxide), $\text{:}\ddot{\text{O}}\text{:}\text{:}\ddot{\text{Cl}}\text{:}\text{:}\ddot{\text{O}}\text{:}$ (chlorine dioxide), and $\text{:}\ddot{\text{O}}\text{:}\text{:}\ddot{\text{O}}\text{:}$ (oxygen) are paramagnetic.

Miscellaneous methods.—In the molecules of N_2O and CO_2 :



each atom has the same external configuration as neon, a nucleus surrounded by an inner shell of two, and an outer shell of eight, electrons. By measurement of the viscosities of the gases, the area offered to collision by the molecules may be calculated, and it is concluded that the CO_2 and N_2O molecules behave not only as if they had the same size and shape, but also as if each had practically the same outer electron configuration as three neon atoms placed together in line.

Information on the outer electron configuration of atoms and molecules is given by the **Ramsauer effect**—the stopping power of the particle for slow-moving electrons. In this way $\text{H}_2(1+1)$ and He, with 2 outer electrons; Ne, Ar, Kr, Xe, $\text{CH}_4(4+4)$ and $\text{HCl}(1+7)$, with 8 outer electrons, behave similarly. In the band spectra also, the effects due to the electrons are alike with H_2 and He; with Na, BeF, BO, CN, CO^+ and N_2^+ (all with 8+1 outer electrons); and with Mg, CO and N_2 (8+2 outer electrons).

Hydrogen compounds.—By analogy with the radioactive displacement law (p. 402), Grimm (1924) suggested that, as the addition of a proton H^+ to the atomic kernel should lead to the same result as the expulsion of an electron, *e.g.* hypothetically $\text{O}^- + \text{H}^+ = \text{F}^-$ (from At. No. 8 of oxygen we arrive at At. No. 9, an isotope of fluorine), so that the actual process $\text{O}^{--} + \text{H}^+ = \text{OH}^-$ leads to a compound OH⁻ similar to the fluorine ion. In this way elements occupying the four places before an inert gas, by taking up 1, 2, 3 and 4 hydrogen atoms, form "pseudo-atoms" which resemble the atoms of elements in the groups 1, 2, 3 or 4 places to the right. This is

illustrated by the following table, in which the compounds, ions or radicals in the same vertical column show similar properties :

		Group →					
H-atoms		IV	V	VI	VII	O	I
0	-	C	N	O	F	No	Na
1	-		CH	NH	OH	FH	
2	-			CH ₂	NH ₂	OH ₂	FH ₂ ?
3	-				CH ₃	NH ₃	OH ₃
4	-					CH ₄	NH ₄
Valency		-4	-3	-2	-1	0	+1

← Radius

↓ Radius

Covalent compounds and salts.—The values of the electrical conductivity at the melting point of the chlorides of groups of elements in the periodic system show that they fall into two classes divided by the line shown below :

HCl						
LiCl	BeCl ₂	BCl ₃	CCl ₄			
NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₅		
KCl	CaCl ₂	SeCl ₃	TiCl ₄	VCl ₄		
RbCl	SrCl ₂	YCl ₃	ZrCl ₄	NbCl ₅	MoCl ₅	
CsCl	BaCl ₂	LaCl ₃	HfCl ₄	TaCl ₅	WCl ₆	
			ThCl ₄			UCl ₄

Those above the line are non-conductors or poor conductors and are covalent, those below the line are electrovalent salts and are good conductors.

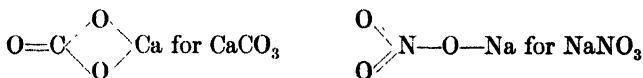
Ionising potentials.—If the electrons emitted from a hot filament in a gas at very low pressure are passed through a fall of potential V , as in the "grid" of a wireless valve, they make collisions with gas atoms or molecules in their path. When the speed of the electrons is small these collisions are elastic. If V is continually increased a point is reached when the speed of the electron of charge e gives it an energy $\frac{1}{2}mv^2 = eV$, such that it makes an inelastic collision with the atom of gas, giving up its energy to one of the outer electrons and raising it to a higher quantum orbit. A critical value of V is reached when the colliding electron gives so much energy to the electron in the atom that the latter is completely removed, *i.e.* ionisation occurs, *e.g.* $K = K^+ + e$.

The values of the ionising potential may be found more accurately by calculation from spectroscopic data. The values of the potentials (in volts) for the removal of successive electrons show that the valency electrons are relatively easily removed : H 13.53 ; Li 5.4, 75.3 ; C 11.2, 24.3, 46.3, 64.1,

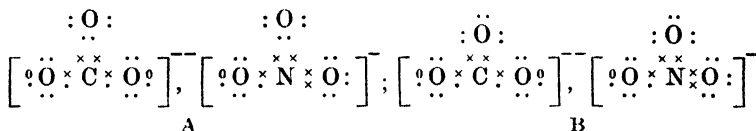
400 ; O 13.6, 35, 55, 77, 109, 137.5 (733) ; P 11, 20, 30, 50, 65 ; Cl 13, 24, 40, 47, 68, 89, 114 ; V 6.75, 14.7, 30, 48, 69, 120 ; Br 12, 15, 25 ; I 10.4 ; S 10.3, 23, 35, 47 ; Se 6.7, 12.8, 24.6 ; Te 9.

Atomic structure and crystal structure.—According to Grimm (1921) isomorphous substances form mixed crystals when : (1) the chemical type is the same (*e.g.* NaCl, PbS ; BaSO₄, KMnO₄) ; (2) the lattice types of the crystals are the same ; (3) the atomic or ionic distances in the crystals are “ similar ”, the necessary degree of similarity depending on the temperature and on the type of linking.

The isomorphism of many substances offered difficulty from the point of view of the old structural formulae, which indicated different constitutions for pairs of isomorphous compounds :



From the point of view of crystal structure this difficulty would disappear if the ions CO₃²⁻ and NO₃⁻ have similar structures, since these can be regarded as forming similar lattices with the ions Ca⁺⁺ and Na⁺. Similarity of structure of the ions is attained in the formulae given to them by Langmuir (A) or Lewis (B), in which the electrons giving the ionic charges are shown as \ominus :

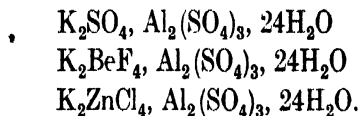


Many similar cases are known. The ions O²⁻ and F⁻ both have completed octets of the neon structure, as have Na⁺ and Mg⁺⁺, and NaF and MgO are isomorphous. These four ions with identical outer electronic configurations are called *isosteres* : a list of cases given by Langmuir of isomorphism based on isosterism is :



Argon and methane have similar physical properties, hence we may assume that the potassium ion, isosteric with argon but having one positive charge, will resemble the positive ammonium ion, isosteric with methane. The potassium ion (cubic) however, is not isosteric with the ammonium ion which, like methane, has tetrahedral symmetry. In KCl crystals, each K⁺ ion is surrounded by six equidistant chlorine ions (see Fig. 221), whilst in NH₄Cl the NH₄⁺ ion is surrounded by eight equidistant chlorine ions arranged like the corners of a cube about its centre (see Fig. 222A). Potassium and ammonium sulphates, however, are isomorphous, so that the larger volume of the sulphate ion constrains the potassium and ammonium ions into like positions.

Isomorphous alums are :



If account is taken of the arrangement of the structural units in the lattice according to the 230 space groups, crystals belonging to one of the 32 symmetry groups (p. 357) may differ in internal structure. The alums then belong to three different structures, α (KAl, NH_4Al , RbAl, TlAl, KCr), β (CsAl) and γ (NaAl), depending on variation in size of the ions. If isomorphism means similar arrangement of geometrically similar structural units, the various alums are not all isomorphous.

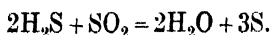
CHAPTER XXVI

SULPHUR

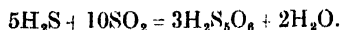
History.—Sulphur was perhaps known to the ancient Egyptians and Babylonians; it occurs in the Dead Sea region and is mentioned in the Bible. It was well known to the Greeks and Romans. The use of burning sulphur in fumigation is mentioned by Homer (c. 900 B.C.), the bleaching of textile fabrics by the fumes was carried out and sulphur was used medicinally. The alchemists regarded sulphur as the *principle of combustibility* and a constituent of metals. The phlogistonists considered it to be a compound of phlogiston and sulphuric acid. Lavoisier (1777) pointed out that it should be regarded as an element.

Occurrence.—Free sulphur occurs in large quantities in the volcanic region of Sicily, and in America in the southern States of Louisiana and Texas which now produce 80 per cent of the total sulphur used in the world. Sulphur deposits are also found in Japan, Russia, Iceland, Chile, and New Zealand.

Sicilian sulphur is stratified with clay and rock, mostly gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, limestone, and celestine SrSO_4 . It is found occasionally in large yellow transparent crystals, but usually in yellow or grey crystalline masses. The sulphur in craters of extinct volcanoes may have been formed by the interaction of volcanic gases containing hydrogen sulphide and sulphur dioxide:



When dry hydrogen sulphide and sulphur dioxide gases are mixed by inverting one jar over the other and removing the plates, no action occurs. If a little water is introduced into the jars it becomes turbid, from separation of *yellow* sulphur. The reaction is complicated and pentathionic acid $\text{H}_2\text{S}_5\text{O}_6$ is also formed:



Since gypsum and calcium carbonate always occur in sulphur beds, the deposits of sulphur in Sicily have probably been formed by the reduction of gypsum by organic matter and bacteria:



Combined sulphur occurs as sulphides, many of which are important ores of metals: lead sulphide *galena* PbS , zinc sulphide *blende* ZnS , *copper pyrites* Cu_2S , Fe_2S_3 , and *iron pyrites* FeS_2 ; and also as sulphates,

e.g. gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Hydrogen sulphide occurs in volcanic gases and in some mineral springs. Sulphur dioxide occurs in volcanic gases. Some springs and rivers in America (Rio Canea and Rio Vinagre) contain free sulphuric acid. Sulphur occurs in some kinds of organic matter; the blackening of silver spoons by eggs is due to this combined sulphur.

Sulphur is found in certain bacteria, *e.g. Beggiatoa alba*, which decompose sulphur compounds in their life processes. The pungent principles of onions, garlic, horse-radish, and mustard are organic sulphur compounds. Combined sulphur is present in hair and wool.

The extraction of native sulphur.—Native sulphur in Sicily, which contains 15 to 25 per cent of sulphur, is stacked in lumps with air spaces in brick kilns called *calcaroni*, built on sloping hillsides and covered

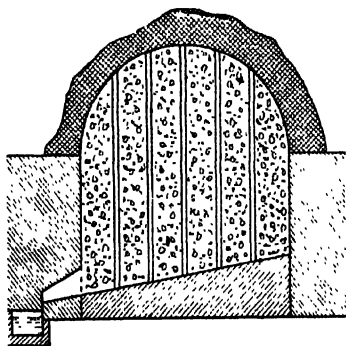


FIG. 248.—Sulphur kiln.

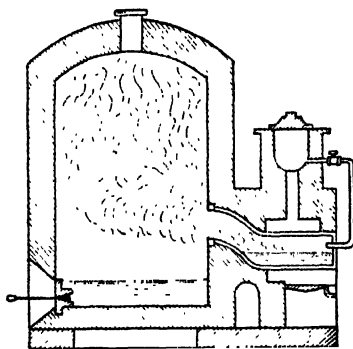


FIG. 249.—Refining of sulphur by distillation.

with powdered ore (Fig. 248). The ore is kindled at the top and the heat of combustion of about 30 per cent of the sulphur serves to melt the rest, which flows off into wooden moulds. The blocks so formed still contain 3 to 5 per cent of the original rock.

An improved process uses the *Gill kiln* (1867) consisting of communicating closed brick chambers; hot gases from a chamber in which the sulphur has been melted out pass into an adjoining chamber and so economise heat. About 75 per cent of the sulphur is recovered. Payen and Gill (1867) proposed to melt out the sulphur with superheated steam.

The crude sulphur is shipped from Sicily (where fuel is scarce) to Marseilles to be refined with the apparatus shown in Fig. 249. The sulphur fused in an iron pot flows into an iron retort. The sulphur vapour passes into a large brickwork chamber. At first it condenses on the cold walls as a light yellow powder of *flowers of sulphur*. As the walls become hot this melts (unless it is removed) and runs down as a

liquid to the bottom, whence it is tapped off into wooden moulds to form *roll sulphur* or *brimstone*.

American sulphur is extracted by the *Frasch process*. The deposit occurs below clay, quicksand and rock. A boring is made to the deposit and a "pump" of concentric pipes is sunk (Fig. 250). Down the outer pipe superheated water is pumped, which fuses the sulphur. Air is forced down the inner pipe, when an emulsion of molten sulphur and air-bubbles rises to the surface through the remaining annular space and passes to large wooden vats, where the sulphur of 99.5 per cent purity solidifies and is ready for immediate use. It contains a little petroleum, which makes it rather difficult to burn.

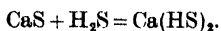
Sulphur was formerly prepared by distilling iron pyrites in clay retorts: $3\text{FeS}_2 = \text{Fe}_3\text{S}_4 + 2\text{S}$ (cf. $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$); or by roasting pyrites in kilns with a limited supply of air: $3\text{FeS}_2 + 5\text{O}_2 = \text{Fe}_3\text{O}_4 + 3\text{SO}_2 + 3\text{S}$. It is more economical to burn the pyrites to sulphur dioxide: $4\text{FeS}_2 + 11\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$, and use this as a source of sulphuric acid. Sulphur is formed by heating metallic sulphides at 1000° in carbon dioxide: $\text{FeS} + \text{CO}_2 = \text{FeO} + \text{CO} + \text{S}$.

Recovered sulphur.—Sulphur is extracted from Leblanc *alkali-waste* (containing insoluble calcium sulphide, CaS) by the *Chance-Claus process*.

Limokiln gas containing carbon dioxide is passed into a suspension of the waste in water in large iron vessels called *carbonators*. Hydrogen sulphide is evolved:



The gas is passed into a second carbonator where the hydrogen sulphide is absorbed as calcium hydrosulphide



The kiln gas is then passed into the second vessel. The $\text{Ca}(\text{HS})_2$ is decomposed:



The gas is mixed with air and passed over porous oxide of iron on a grating in the *Claus kiln*—a brickwork chamber with large brick condensing chambers and flues beyond. The oxide is heated to start the reaction which then proceeds automatically:

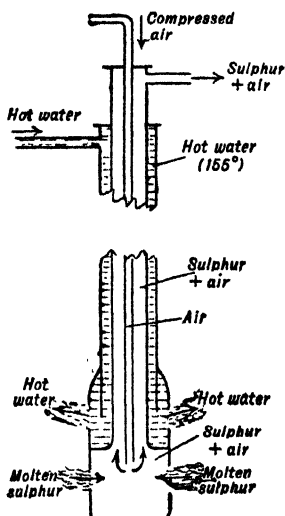
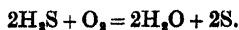


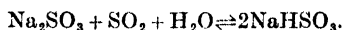
FIG. 250.—Frasch sulphur pump.

The oxide of iron is unchanged and acts as a catalyst. The recovered sulphur is very pure.

Coal contains pyrites FeS_2 , about half the sulphur of which during distillation in the manufacture of coal gas comes off as hydrogen sulphide and carbon disulphide. The sulphur of the hydrogen sulphide is recovered (p. 613) in iron oxide. The *spent oxide*, which contains about 50 per cent of free sulphur, is then burnt in a current of air to produce sulphur dioxide, which is used to make sulphuric acid.

Some sulphur is recovered from the sulphur dioxide of metal roaster and smelter gases by dissolving in a suitable solvent, expelling the sulphur dioxide, and passing it over white-hot coke: $\text{SO}_2 + \text{C} = \text{CO}_2 + \text{S}$.

The solvent may be a cold solution of sodium sulphite containing aluminium chloride, and the gas is evolved on heating:



Uses of sulphur.—*Rude sulphur* is used for making sulphur dioxide and thence sulphuric acid, for bisulphites for paper manufacture, and carbon disulphide. *Refined sulphur* is used in medicine, in the form of powder as a fungicide, and in the preparation of gunpowder, matches, fireworks and dyes. Sulphur is also used in large quantities for vulcanising rubber.

For use in dressing vines (to prevent the growth of the fungus *Oidium*), sulphur is finely ground between millstones and sieved through silk. By blowing a current of air through the mill, the very finest particles ("winnowed sulphur") are carried off and are retained by cloth filters.

Allotropic forms of sulphur.—Sulphur is *dimorphous* and exists in two common crystalline forms: α -sulphur or rhombic sulphur, and β -sulphur or monoclinic sulphur. There are also amorphous forms such as γ -sulphur or plastic sulphur.

Rhombic or α -sulphur crystallises in large pale-yellow transparent crystals (Fig. 251), giving a lemon-yellow powder, when a solution of roll sulphur in carbon disulphide is allowed to evaporate slowly in a dish covered with filter-paper. The density of α -sulphur is 2.06, its melting point is 112.8° . It is insoluble in water and only very slightly soluble in alcohol and ether, but is freely soluble in carbon disulphide, sulphur chloride (S_2Cl_2) and hot benzene and turpentine. *Rhombic sulphur is the form stable at the ordinary temperature and most other forms pass into it on standing.*

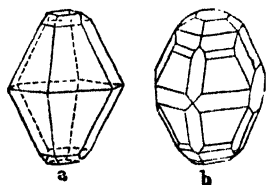


FIG. 251.—Crystals of rhombic sulphur.

Roll sulphur consists almost entirely of rhombic sulphur; flowers of sulphur contain 70 per cent of it, but when genuine contain also a yellowish-white amorphous variety insoluble in carbon disulphide.

X-rays show that the S_α crystals contain S_8 molecules (also present in the vapour and in solution) consisting of zig-zag octagonal rings (Fig. 252), with sixteen S_8 molecules in the unit cell of the crystal.

Monoclinic or β -sulphur, discovered in 1823 by Mitscherlich, is produced when fused sulphur is allowed to crystallise.

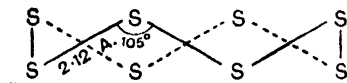


FIG. 252.—Structure of S_8 molecule.

A large porcelain crucible is nearly filled with small pieces of roll sulphur, and heated *gently* on a sand-bath till the whole is just fused. It is allowed to cool until a crust forms on the surface. Two holes (one to admit air) are pierced in this crust with a pointed glass rod, and the still liquid portion poured out into a dry porcelain dish. On removing the crust, the inside of the crucible will be found to be lined with transparent needle-shaped crystals (Fig. 253) of β -sulphur, usually deeper yellow in colour than α -sulphur. On standing for a few days the crystals become opaque brittle lemon-yellow aggregates of minute crystals of α -sulphur, although the original monoclinic form is preserved and the crystal is therefore called a *pseudomorph*. The transition from one form to the other is readily followed by the colour.

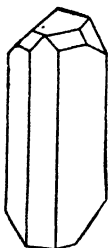


FIG. 253.—Crystal of monoclinic sulphur.

(Genuine Sicilian roll sulphur should be used for these experiments, since American sulphur may contain a trace of petroleum which results in dark coloured and unsatisfactory products.)

β -sulphur when quickly heated melts at 119° ; its density is 1.96. It is soluble in carbon disulphide and the solution on evaporation deposits α -sulphur.

The transformation of S_β into S_α is reversible; below 96° S_α is the stable form and above 96° S_β . This temperature is the transition temperature (or transition point) of sulphur. At the transition temperature the two crystalline forms are in equilibrium: $S_\alpha \rightleftharpoons S_\beta$.

Substances like sulphur and tin (p. 827) which exist in *two* forms one of which is stable below a certain temperature and the other stable above it, are called *enantiotropic*; substances like phosphorus (p. 565) and iodine monochloride (p. 332) which exist only in *one* stable form, the other forms being unstable or metastable in all circumstances, are called *monotropic* (Greek *monos* one, *enantios* opposite, *tropos* habit).

A second variety of monoclinic sulphur, deposited in pearly leaflets from a hot solution of sulphur in benzene or toluene on rapid cooling, was called *nacreous sulphur* by Gernez and is monotropic. It is also formed by cooling sulphur fused at 160° in a tube to 98° and scratching the inside of the tube with a platinum wire.

Sulphur vapour.—Sulphur boils at 444.6° and forms a deep red vapour which when strongly heated becomes yellow. Dumas (1832) found the vapour density at 524° to correspond with S_6 , but the vapour was probably a mixture of S_8 and S_2 ; at higher temperatures

the density falls and at 1000° corresponds with S_2 . Nernst found that 45 per cent of the S_2 molecules were broken up into atoms at 2000° : $S_2 \rightleftharpoons 2S$. Biltz (1888) and Bleier and Kohn (1900) found densities higher than S_7 at lower temperatures (*e.g.* 193° at 2 mm.), and concluded that at lower temperatures the molecule is S_8 , partly dissociated even at the boiling point: $S_8 \rightleftharpoons 4S_2$. Vapour densities at 80° under low pressures gave S_8 for S_α and S_β , and a smaller molecule, probably S_4 , for S_μ (p. 454). The lowering of vapour pressure of carbon disulphide by dissolved rhombic sulphur gives the formula S_8 , but S_6 and S_4 have been given for S_ϕ and S_π (p. 454).

Pure sulphur.—H. B. Baker purified sulphur by heating the vapour with S_2Cl_2 at 450° , when the hydrogen present as impurity forms H_2S , which reacts with S_2Cl_2 to form HCl and S . The S_2Cl_2 and HCl were removed by heating *in vacuo*, and the sulphur left was so pure that it could be distilled unchanged in oxygen dried over phosphorus pentoxide.

Equilibrium between rhombic and monoclinic sulphur.—In Fig. 254 *OP* is the vapour pressure curve of α -sulphur and represents the

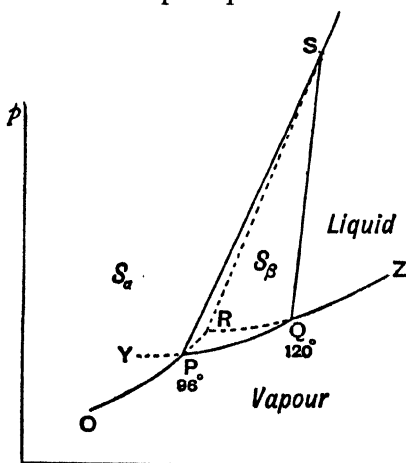


FIG. 254.—Vapour pressure diagram for sulphur.

pressures of sulphur vapour in equilibrium with solid S_α at various temperatures. *P* is the transition point of α - and β -sulphur, where α - and β -sulphur and vapour are in equilibrium, and is a *triple point*; the three "phases" can co-exist only at one temperature and pressure. *Q* is the melting point of β -sulphur and is another *triple point* where β -sulphur, liquid and vapour are in equilibrium. *QZ* is the vapour pressure curve of liquid sulphur.

If α -sulphur is heated rapidly the slow transition into β -sulphur at *P* will not occur but the curve *PR* will be followed to the point *R*, which is the melting point of α -sulphur (113°); at this point α -sulphur, liquid and vapour co-exist, so that *R* lies in the prolongation of the curve *ZQ*. The point *R* lies in a *metastable* region since α -sulphur is not a stable phase above 96° . Below 96° α is stable and β unstable but above 96° β is stable and α unstable. But S_β may exist in a metastable condition below 96° because the change $S_\beta \rightarrow S_\alpha$ takes place only slowly. The prolongation of *QP* to *Y* expresses this fact, *PY* being the vapour pressure curve of S_β at temperatures below 96° . The melting points of α - and β -sulphur are raised by pressure but at different rates. This is repre-

sented by two lines starting from P and Q with different slopes and meeting ultimately at S (151° ; 1288 atm.) where S_α , S_β and liquid are in equilibrium. (The slopes of the lines PS and QS are much exaggerated in Fig. 254 and they are actually nearly parallel, so that their point of intersection S would be at a great distance above the t axis if the figure were drawn to scale). Above the point S , S_β cannot exist, the region of its stable existence being confined to the area PSQ . The areas defining the regions of existence of S_α , S_β , liquid and vapour are marked. If S_α is kept at a temperature between 96° and 113° for a long time and then heated, it will not melt at 113° but at 120° , since it has been converted into S_β .

Plastic sulphur.—The changes which occur when sulphur is slowly heated to its boiling point are most remarkable.

When small pieces of genuine roll sulphur are slowly and carefully heated in a large test-tube, they melt to a clear yellow mobile liquid. On cooling rapidly by pouring in water, S_β is produced. If the temperature is now *gradually* raised and the tube shaken, the orange-red liquid *suddenly* becomes very viscous at 180° – 190° . At 230° the liquid is black and viscous. Beyond 230° the viscosity decreases but the colour remains dark, and the sulphur finally boils at 444.6° . If the boiling sulphur is allowed to cool *slowly* it passes through the above series of changes of colour and viscosity in the reverse order, solidifying as β -sulphur. But if the boiling liquid is *quickly* cooled by being poured into cold water it forms soft rubber-like transparent yellow threads, called plastic sulphur or γ -sulphur (Fig. 255).



FIG. 255.—Plastic sulphur.

Plastic sulphur has a density 1.92 and is insoluble in carbon disulphide. On standing for a few days it forms an opaque brittle pale-yellow solid consisting partly of rhombic sulphur, but some of the solid is insoluble in carbon disulphide and consists of an amorphous variety called S_μ . At 100° the change takes place more rapidly.

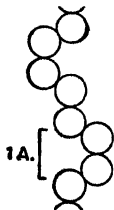


FIG. 256.—Structure of plastic sulphur.

Plastic sulphur (mentioned by Baumé in 1773) is amorphous but (like rubber) it shows an X-ray "fibre" diagram when stretched, suggesting that it contains long chains of sulphur atoms parallel to the direction of stretching (Fig. 256).

The plastic sulphur is obtained only if slightly impure sulphur, which has been exposed to air and contains a trace of sulphuric acid, is used. If ammonia gas is passed through the boiling sulphur, no plastic sulphur

is formed on rapid cooling. In liquid sulphur two forms S_λ and S_μ exist in equilibrium at various temperatures: $S_\lambda \rightleftharpoons S_\mu$; the percentages of S_μ are: at 120° , 3.6; 160° , 11; 444.6° , over 30. S_λ is the form giving monoclinic sulphur on cooling, while S_μ gives plastic sulphur.

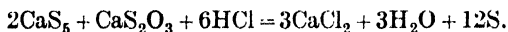
The rate of conversion of S_μ into S_λ on cooling is greatly increased by ammonia, which acts as a positive catalyst for the change $S_\mu \rightarrow S_\lambda$. Sulphur dioxide, sulphuric acid and traces of iodine retard the change, acting as negative catalysts and so promoting the formation of S_μ on cooling, since they stabilise this form.

White sulphur.—An amorphous white sulphur remains as a pale-yellow powder when genuine "flowers of sulphur" are extracted with carbon disulphide; it is also formed when a solution of sulphur in carbon disulphide is exposed to sunlight, or by the decomposition of sulphur chloride by water. It is probably a form of S_μ .

Powdered roll sulphur when boiled with milk of lime dissolves to form calcium pentasulphide and calcium thiosulphate:



The reddish-yellow solution is filtered. It was known to the early alchemists as *theion hudor* (the "divine" or "sulphurous" water). When it is acidified with dilute hydrochloric acid a white amorphous precipitate of milk of sulphur (*lac sulphuris*) is formed and hydrogen sulphide is evolved:



Milk of sulphur, which is used medicinally, is soluble in carbon disulphide. It is a form of S_λ .

Colloidal sulphur is formed in the preparation of milk of sulphur: the filtered liquid is a turbid emulsion of sulphur. The milky liquid obtained by passing hydrogen sulphide into a solution of sulphur dioxide deposits on evaporation a gum-like mass, part of which is soluble in water (Debus, 1888).

Colloidal sulphur is obtained by the interaction of sodium thiosulphate solution and concentrated sulphuric acid. It is precipitated from the solution by addition of sodium chloride and centrifuging, and redissolves in water (Odén, 1913).

Other forms of sulphur.—Other varieties of sulphur described are S_π and S_ϕ (or S_ρ). S_π is obtained when sulphur is heated to about 180° and rapidly cooled; the solution of the solid in CS_2 when cooled to -80° deposits S_λ , and S_π is obtained by evaporating the remaining solution in a vacuum at -80° . In solution in toluene or carbon disulphide S_π has a deep-yellow colour. In solution it exists as S_4 . S_ϕ is said to be produced when to concentrated hydrochloric acid at 0° a cold solution of sodium thiosulphate is added and the mixture shaken with toluene. After a short time orange-yellow rhombohedral crystals of S_ϕ separate from the toluene, having a distinct form and solubility. The solutions of S_ϕ are yellow, but not so strongly as those of S_π . In solution it exists as S_8 .

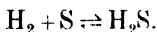
Two other forms, S_8 (rhombic plates) and S_7 (hexagonal plates), nearly colourless, are formed by crystallising from a solution of sulphur in chloroform containing rubber and a little benzonitrile (Korinth, 1928).

Hydrogen sulphide.—Sulphur and hydrogen form a gaseous compound H_2S , called *hydrogen sulphide* (or "sulphuretted hydrogen"), and several liquid *hydrogen polysulphides* H_2S_2 , H_2S_3 , H_2S_4 , H_2S_5 and H_2S_6 .

Although hydrogen sulphide was known by its smell to the alchemists the gas was first carefully examined by Scheele in 1777; he proved that it is a compound of hydrogen and sulphur.

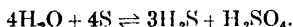
Hydrogen sulphide occurs in volcanic gases and in some mineral waters, e.g. of Harrogate, Aix-la-Chapelle, etc. It is formed in the putrefaction of organic substances containing sulphur and contributes to the smell of rotten eggs and sewer gas.

When hydrogen is passed over boiling sulphur in a bulb-tube the issuing gas contains a small amount (1 or 2 per cent.) of hydrogen sulphide and blackens lead acetate paper owing to the formation of lead sulphide PbS . If pure hydrogen sulphide is heated partial decomposition occurs with deposition of sulphur, hence the reaction is reversible :



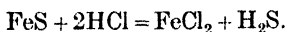
The pure gas is prepared synthetically in presence of pumice as a catalyst at 600° , when the reaction is practically complete.

Traces of hydrogen sulphide are formed when sulphur is boiled with water:



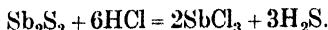
The gas is formed when heavy naphtha (sp. gr. 0.9) is dropped into boiling sulphur in a flask, and is evolved in a regular stream on heating a mixture of powdered sulphur, paraffin wax and ignited asbestos. Hydrogen in the hydrocarbons is substituted by sulphur (S replaces 2H).

Hydrogen sulphide is usually prepared in the laboratory by the action of dilute sulphuric acid, or better hydrochloric acid (1 : 3), on ferrous sulphide in a Kipp's apparatus :

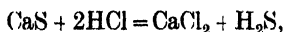


The gas is washed with a little water before use. Since the ferrous sulphide contains free iron the gas contains hydrogen, which does not interfere with its use in qualitative analysis.

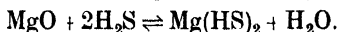
Hydrogen sulphide free from hydrogen is obtained by heating powdered antimony sulphide (*stibnite*) with concentrated hydrochloric acid :



The pure gas is obtained from pure zinc sulphide or calcium sulphide and hydrochloric acid :



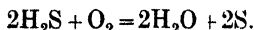
or by heating to 60° a solution of magnesium hydrosulphide obtained by passing the impure gas into a suspension of magnesia in water :



Hydrogen sulphide may be dried with calcium chloride or phosphorus pentoxide ; it reacts with concentrated sulphuric acid : $\text{H}_2\text{S} + \text{H}_2\text{SO}_4 = \text{S} + \text{SO}_2 + 2\text{H}_2\text{O}$. It is collected in dry jars by displacement (it is 1.2 times as heavy as air) since it is soluble in water (3.4 vols. to 1 vol. water at 10°) and tarnishes mercury unless it is dry and free from oxygen.

Hydrogen sulphide is a colourless gas with a powerful odour of rotten eggs (decaying albumin evolves H_2S) and is poisonous. It liquefies fairly easily to a colourless liquid, b. pt. -60.7° (vapour pressure at $12^\circ = 15$ atm., critical temperature 100.4° , critical pressure 89.05 atm). At lower temperatures it forms a transparent solid, m. pt. -85.6° .

Hydrogen sulphide is soluble in water (4.37 vols. at 0° , 3.40 vols. at 10° , 2.6 vols. at 20°) and alcohol (9.54 vols. at 15°). The aqueous solution is a feeble acid ; the gas is completely expelled by boiling, and on standing in air the solution becomes turbid owing to oxidation and deposition of sulphur :



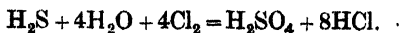
This is retarded by the addition of 1 ml. of glycerol to 50 ml. of saturated solution. In decinormal solution 0.1 per cent is ionised to H^+ + HS' ; the further stage to S'' is very slight :

$$\begin{aligned} [\text{H}^+][\text{HS}']/[\text{H}_2\text{S}] &= 9.1 \times 10^{-8} \\ [\text{H}^+][\text{S}'']/[\text{HS}'] &= 1.2 \times 10^{-15}. \end{aligned}$$

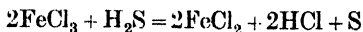
A solid crystalline hydrate with 5 or 6 H_2O is formed at low temperatures.

The gas is decomposed into its elements by electric sparks or by a heated platinum spiral : $\text{H}_2\text{S} = \text{H}_2 + \text{S}$, and by heated tin or lead, giving its own volume of hydrogen : $\text{H}_2\text{S} + \text{Sn} = \text{H}_2 + \text{SnS}$. Its density corresponds with the molecular weight 34. Of this one molecule of hydrogen per molecule of gas accounts for 2, and hence the sulphur is $34 - 2 = 32$, which is the atomic weight ; hence the formula is H_2S .

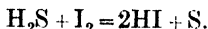
Chlorine decomposes hydrogen sulphide and sulphur is deposited : $\text{H}_2\text{S} + \text{Cl}_2 = 2\text{HCl} + \text{S}$, but sulphur chloride is also formed. A solution of hydrogen sulphide gives a precipitate of sulphur with chlorine water, but with a large excess of chlorine water it slowly forms sulphuric acid :



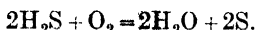
Hydrogen sulphide is easily oxidised and acts as a reducing agent in aqueous or alcoholic solution. It reduces solutions of ferric chloride, potassium permanganate and potassium dichromate :



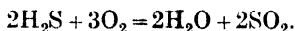
Hydrogen sulphide may be determined by titration in dilute solution (not more than 0.04 per cent of H_2S) with iodine solution :



The gas kindled in air or oxygen burns with a blue flame ; the ignition point in air is 364° . The gas is completely dissociated in the interior of the flame, which deposits sulphur on a cold porcelain dish. If the gas in a glass cylinder is kindled at the mouth a deposit of sulphur is formed on the inside of the jar, owing to the deficiency of oxygen :

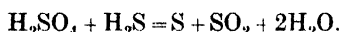


With a plentiful supply of oxygen, as when the gas burns at a jet in air, sulphur dioxide is formed :

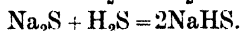
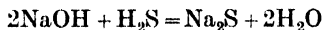


A mixture of 2 vols. of H_2S and 3 vols. of oxygen explodes violently when kindled.

The gas decomposes concentrated sulphuric acid :



It is absorbed by solutions of alkali hydroxides, and by slaked lime, forming sulphides and hydrosulphides :



Fuming nitric acid reacts violently with the gas, ignition and perhaps explosion occurring. Very dilute (5 per cent) nitric acid is not affected ; with more concentrated acid (43 per cent) the products are sulphuric acid, sulphur, ammonia, nitrous acid, nitric oxide and nitrous oxide. A solution containing 23 per cent of nitric acid and 15 per cent of sulphuric acid is inert towards the gas, whether prepared by mixing or by the reaction itself.

The gas or its solution (*e.g.* in mineral waters) may be detected by the black coloration due to lead sulphide PbS , produced with lead acetate. Alkali sulphides give a purple colour, not produced by free H_2S , with a freshly-prepared solution of sodium nitroprusside $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5$.

Precipitation of sulphides.—Hydrogen sulphide precipitates sulphides from solutions of salts of many metals. These sulphides often have

characteristic colours, and hydrogen sulphide is used as a reagent in qualitative analysis.*

The sulphides of Group II metals are precipitated from solutions acidified with hydrochloric acid: copper, lead, mercuric and bismuth salts all give *black* sulphides (bismuth, brownish-black), CuS , PbS , HgS , Bi_2S_3 ; cadmium, tin (stannic) and arsenic give *yellow* sulphides, CdS , SnS_2 , As_2S_3 ; antimony gives an *orange-red* sulphide Sb_2S_3 ; tin (stannous) a *brown* sulphide SnS .

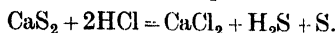
Group IV metals are precipitated only in *alkaline* solutions. An alkali sulphide, e.g. ammonium sulphide, may be used. The precipitates are black (FeS , CoS , NiS), white (ZnS), and flesh-coloured or greenish (MnS).

If the sulphides are very sparingly soluble (PbS , CuS , HgS , As_2S_3 , Sb_2S_3 , etc) the concentration of S'' ions formed from them is never large enough, even with relatively high concentrations of H^+ ions, to give an ionic product $[\text{H}^+]^2 \times [\text{S}'']$ exceeding the solubility product of H_2S , so that the latter cannot be formed. In other words, the sulphides are precipitated even in the presence of acids. Cadmium sulphide CdS occupies an intermediate position; if the acid concentration is greater than 1.3*N* it is not precipitated. Zinc salts are incompletely precipitated from neutral solutions, since the acid formed leads to an equilibrium state: $\text{ZnSO}_4 + \text{H}_2\text{S} \rightleftharpoons \text{ZnS} + \text{H}_2\text{SO}_4$. Sulphides of some metals (FeS , ZnS , MnS) are precipitated in alkaline solution, because then practically no H^+ ions are formed. The metals of the alkalis and alkaline earths are not precipitated, because their sulphides are soluble in water (Na_2S , K_2S) or in a solution of hydrogen sulphide ($\text{CaS} + \text{H}_2\text{S} \rightleftharpoons \text{Ca}(\text{HS})_2$). Aluminium and chromium salts give precipitates of *hydroxides* with ammonium sulphide, since their sulphides are completely hydrolysed by water: $2\text{Al}''' + 3\text{S}'' + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{S}$.

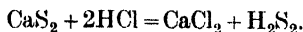
The precipitation of sulphides is complicated by the occurrence of modifications with different solubilities. Cobalt and nickel sulphides are not precipitated by hydrogen sulphide from acid solutions, but when the precipitates have been formed by ammonium sulphide in alkaline solution they are insoluble in dilute acids. Two modifications of zinc sulphide are precipitated, one (α - ZnS) in acid solution and another (β - ZnS) in alkaline solution, the second form having five times the solubility of the first. In acid solutions the precipitation of zinc sulphide shows a period of induction which is longer the more acid is the solution. In some cases no precipitate is formed, although zinc sulphide is almost insoluble in the strength of acid used. Other sulphides, e.g. CuS and CdS , however, bring about simultaneous precipitation of the zinc sulphide.

* On the theory of sulphide precipitation, see p. 313.

Hydrogen persulphides.—If an acid is added to the yellow *theion hudson* (p. 454), which contains polysulphides of calcium CaS_2 and probably CaS_5 , hydrogen sulphide is evolved and white colloidal sulphur is formed, slowly depositing as milk of sulphur :



Scheele (1777) found that if the calcium polysulphide solution is poured in a thin stream into cold fairly concentrated hydrochloric acid, with constant stirring, a yellow oil separates, which Thenard (1831) regarded as hydrogen persulphide H_2S_2 , analogous to H_2O_2 .



Boil 2 parts of powdered sulphur with 13 of water and 1 part of lime slaked with 3 of water, and decant the clear deep reddish-yellow liquid : $3\text{Ca}(\text{OH})_2 + 12\text{S} = 2\text{CaS}_5 + \text{CaS}_2\text{O}_3 + 3\text{H}_2\text{O}$. Acidify the solution, when a white precipitate of sulphur is formed and hydrogen sulphide evolved.

To 250 ml. of a cooled mixture of equal volumes of concentrated HCl and water in a beaker add in a thin stream, with vigorous stirring, 100 ml. of *theion hudson*. Insert a piece of litmus paper into the milky liquid and notice that it is bleached. Pour the liquid into a separating funnel. After a few hours a yellow oil, heavier than water, separates.

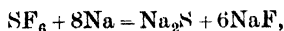
The oil, density 1.7, has a pungent smell, is soluble in benzene and carbon disulphide, but sparingly soluble in and decomposed by alcohol. It slowly decomposes spontaneously, especially on warming, into hydrogen sulphide and a residue of sulphur. If sealed up in a bent tube, liquid H_2S collects in one limb cooled in a freezing mixture, and sulphur remains in the other. The composition of the oil is variable, since the sulphur formed on decomposition dissolves in the remaining persulphide. Some chemists considered it to be H_2S_5 .

Sabatier (1885) separated the crude persulphide into fractions by distillation under reduced pressure ; under 40-100 mm. pressure the chief fraction had a composition intermediate between H_2S_2 and H_2S_3 . Sabatier concluded that it was H_2S_2 + dissolved sulphur. Bloch and Höhn (1908) separated the crude oil dried by calcium chloride by distillation in small portions under reduced pressure. Since alkali decomposes hydrogen persulphides the glass apparatus was washed with concentrated hydrochloric acid, and the calcium chloride treated with hydrogen chloride gas. Two volatile fractions were obtained. In the first receiver hydrogen trisulphide, a pale yellow liquid, density 1.496, b. pt. 43° – $50^\circ/4.5$ mm., m. pt. -52° to -53° collected ; in a further, strongly cooled, receiver hydrogen disulphide, H_2S_2 , a yellow liquid, density 1.327, b. pt. 74° to 75° , quickly decomposed by water and alkalis, was obtained.

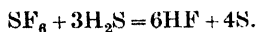
Fehér and Baudler (1947) showed that crude hydrogen persulphide does not contain H_2S_2 and H_2S_3 , which are formed from higher persulphides by decomposition during distillation. The main component of the crude oil is probably H_2S_5 or H_2S_4 . They obtained H_2S_4 (a bright-yellow oil, density 1.588, more stable than H_2S_2 or H_2S_3), H_2S_5 (bright yellow, more viscous than olive oil, density 1.660), and H_2S_6 (more intensely yellow and more viscous than H_2S_5 , density 1.669) by "molecular distillation" of the oil in thin layers in a high vacuum.

The hydrogen polysulphides probably contain chains of sulphur atoms; the disulphide ion in salts is $[S-S]''$ and the trisulphide ion is bent $\left[\begin{array}{c} S \\ \diagdown \quad \diagup \\ S \quad S \end{array} \right]''$ with the S—S length 2.15 Å. and angle 103° .

Halogen compounds of sulphur.—Sulphur burns spontaneously in fluorine producing colourless gaseous sulphur hexafluoride SF_6 (Moissan and Lebeau, 1900). This contains 6-valent sulphur, the sulphur atom having an outer shell of twelve valency electrons. The density of the gas corresponds with the formula SF_6 . It solidifies at -50.8° . The gas is chemically inert like nitrogen, but is decomposed by boiling sodium :



and by hydrogen sulphide :



Fused potassium hydroxide and ignited lead chromate or copper, have no action upon it.

The sulphur hexafluoride molecule is octahedral, with the sulphur atom in the centre and six fluorine atoms at the six corners (see p. 504).

A small amount of S_2F_{10} , m. pt. -92° , b. pt. $+29^\circ$, is formed by the action of fluorine on sulphur (Denbigh and R. Whytlaw-Gray, 1934). Sulphur monofluoride S_2F_2 is obtained as a colourless gas, b. pt. -99° , m. pt. -105.5° , by heating silver fluoride with sulphur : $2AgF + 3S = Ag_2S + S_2F_2$. A gaseous sulphur tetrafluoride SF_4 , b. pt. -40° , m. pt. -124° , is formed by heating sulphur with cobaltic fluoride : $4CoF_3 + S = 4CoF_2 + SF_4$. It is decomposed by water.

Sulphur monochloride S_2Cl_2 is prepared by passing dry chlorine over sulphur fused in a retort (T. Thomson, 1804). A red liquid distils into a cooled receiver (Fig. 257). By rectification of this over powdered sul-

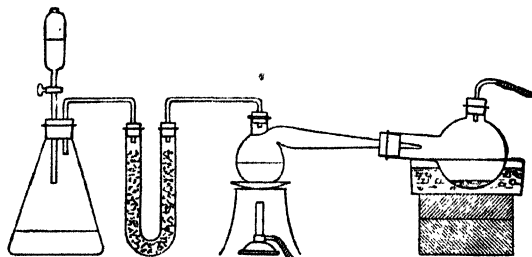
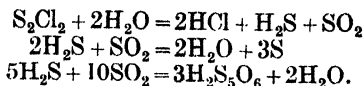


FIG. 257.—Preparation of sulphur monochloride.

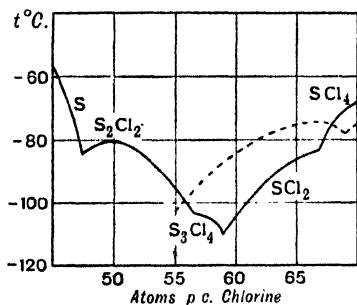
phur, or by allowing it to stand over active charcoal, an excess of chlorine is removed, and a clear amber-coloured liquid, density 1.706, b. pt. 138° , is obtained, which solidifies on strong cooling, m. pt. -80° .

Sulphur monochloride has a vapour density 67.6, corresponding with S_2Cl_2 ($\Delta = 67.0$), but the liquid dissociates slightly on boiling. It fumes in moist air and has a most disagreeable pungent odour. The liquid is only slowly decomposed by water; hydrochloric acid and sulphur are formed, together with various oxy-acids of sulphur (*e.g.* pentathionic acid). The stoppers of bottles in which it is kept become coated with sulphur owing to hydrolysis :



Metals decompose sulphur chloride on heating, forming chlorides and sulphides. Sulphur chloride dissolves sulphur readily (66 per cent), also iodine, many halide salts of metals, and organic compounds. The salt solutions are poor conductors, and on account of its small dielectric constant (4.9) the liquid has only a slight ionising power. Sulphur chloride forms a compound $S_2Cl_2 \cdot 4HCl$ with dry hydrogen chloride.

When saturated with chlorine at room temperature sulphur monochloride forms a ruby-red liquid containing SCl_2 , sulphur dichloride, but this decomposes on distillation. At -22° chlorine and the monochloride produce sulphur tetrachloride, SCl_4 . This freezes to a yellowish-white solid, melting at -30° . On taking the liquid out of the freezing mixture it decomposes. Stable crystalline double compounds, *e.g.* $SbCl_5 \cdot SCl_4$, are known. Lowry, McHatton and Jones (1927) found that samples of chlorinated sulphur chloride after heating in a sealed tube at 100° gave freezing-point curves with maxima corresponding with S_2Cl_2 and SCl_4 , also breaks attributed to the crystallisation of SCl_2 and a new chloride

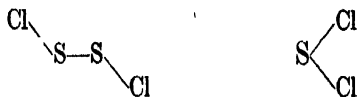


--- ($S_2Cl_2 + SCl_2$) over-chlorinated fresh
 — ditto previously heated at 100°

The sulphur-chlorine system.

S_3Cl_4 . Although an equilibrium mixture having the composition SCl_4 deposits SCl_4 on freezing, freshly prepared mixtures of S_2Cl_2 with an over-chlorinated sample of sulphur dichloride gave a temporary maximum freezing-point corresponding with $SCl_4 : SCl_4 + S_2Cl_2 = 3SCl_2$, followed on standing by $2SCl_2 = S_2Cl_2 + Cl_2$. Solid SCl_2 can be frozen out of the fresh mixture and crystallised from light petroleum by cooling in liquid air.

The structures of the S_2Cl_2 and SCl_2 molecules, as determined by electron diffraction, are :



the angles being 105° (Cl—S—S) and 103° (Cl—S—Cl) respectively.

Sulphur monobromide S_2Br_2 , is a garnet-red liquid, b. pt. $57^\circ/0.22$ mm., m. pt. -46° , obtained by heating sulphur with bromine in a sealed tube.

The so-called iodides of sulphur are mixtures of the elements.

CHAPTER XXVII

OXYGEN COMPOUNDS OF SULPHUR

The following oxides and oxy-acids of sulphur are known :

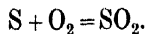
Sulphur monoxide	SO	Sulphur trioxide	SO ₃
Disulphur trioxide	S ₂ O ₃	Disulphur heptoxide	S ₂ O ₇
Sulphur dioxide	SO ₂	Sulphur tetroxide	SO ₄
Hyposulphurous acid	H ₂ S ₂ O ₄		
Sulphurous acid	H ₂ SO ₃	Dithionic acid	H ₂ S ₂ O ₆
Sulphuric acid	H ₂ SO ₄	Trithionic acid	H ₂ S ₃ O ₆
Thiosulphuric acid	H ₂ S ₂ O ₃	Tetrathionic acid	H ₂ S ₄ O ₆
Disulphuric acid	H ₂ S ₂ O ₇	Pentathionic acid	H ₂ S ₅ O ₆
Perdisulphuric acid	H ₂ S ₂ O ₈	Hexathionic acid	H ₂ S ₆ O ₆
Permonosulphuric acid	H ₂ SO ₅		

SULPHUR DIOXIDE

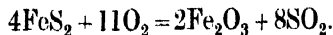
History.—Homer refers to the use of burning sulphur in fumigation and Pliny states that the fumes were used for purifying cloth (*i.e.* bleaching). The alchemists thought the pungent fumes were oil of vitriol, but Stahl (1703) showed that they gave peculiar salts with alkalis, and since they stood halfway between sulphuric (vitriolic) acid and sulphur (the latter regarded as sulphuric acid + phlogiston), his followers called the acid *phlogisticated vitriolic acid*. Priestley (1774) obtained gaseous sulphur dioxide by heating concentrated sulphuric acid with mercury and collected it over mercury. He called it *vitriolic acid air*. Its composition was determined by Lavoisier in 1777.

Occurrence.—Sulphur dioxide occurs in volcanic gases and traces are present in the atmosphere, being derived from the combustion of iron pyrites contained in coal, and produced in various metallurgical and chemical processes.

Preparation.—Sulphur dioxide is formed (together with a little trioxide) when sulphur burns in oxygen :



It is also formed (*mixed with atmospheric nitrogen*)* when sulphur or iron pyrites burns in air :



* It is a very common error to give this as a laboratory preparation of sulphur dioxide.

When sulphur is heated in air it fuses, and as the temperature rises a very gentle combustion begins, accompanied by a faint glow visible only in a dark room. This is due to the oxidation of sulphur vapour, which is evolved appreciably at about 230°. At about 363° in air (275°–280° in oxygen) the sulphur ignites and burns with a blue flame, producing

sulphur dioxide SO_2 and a little solid sulphur trioxide SO_3 , which renders the gas cloudy.

Sulphur burns in a confined volume of oxygen or air without causing appreciable change of volume, *i.e.* sulphur dioxide contains its own volume of oxygen.

A small piece of sulphur in a metal spoon is kindled in dry oxygen over *dry* mercury in the apparatus shown in Fig. 258 by means of a piece of fine platinum wire heated electrically in contact with the sulphur. When the apparatus is cool, the mercury levels are practically unchanged.

The density of sulphur dioxide gives the approximate molecular weight 64. The experiment shows that this contains a molecular weight of oxygen, $\text{O}_2 = 32$,

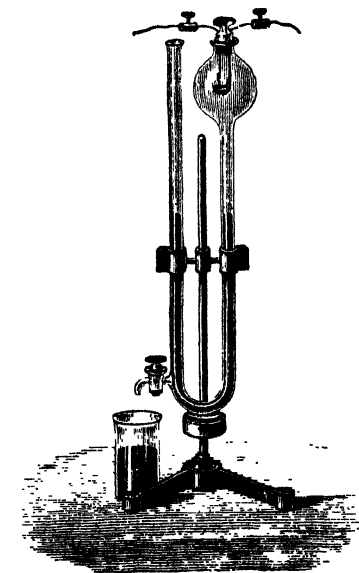
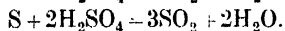
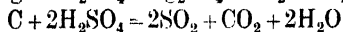
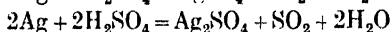


FIG. 258.—Volumetric composition of sulphur dioxide.

hence the remainder, $64 - 32 = 32$, is the weight of sulphur. But this is the atomic weight, hence the formula is SO_2 .

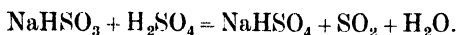
Sulphur dioxide gas is usually made in the laboratory by heating concentrated sulphuric acid with copper turnings. The acid is also reduced when heated with mercury, silver, or charcoal; reaction with sulphur is very slow:



Copper turnings covered with concentrated sulphuric acid are heated on wire gauze in a flask fitted with a thistle funnel and delivery tube. The mixture becomes dark and gas is evolved with effervescence. When this occurs the flame is lowered or removed. The gas is collected by downward displacement or over mercury. It may be dried by concentrated sulphuric acid, calcium chloride, or phosphorus pentoxide. After cooling, the residue in the flask may be warmed with water, and the solution

filtered, evaporated and set aside. Deep-blue crystals of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (*blue vitriol*) separate.

Sulphur dioxide is evolved by the action of acids on sulphites or acid sulphites, *e.g.* by dropping concentrated sulphuric acid into a concentrated solution of sodium hydrogen sulphite :



Sulphur dioxide is also formed in a number of reactions when sulphides or sulphur are exposed to oxidising agents. On the large scale the mixture of sulphur dioxide and nitrogen formed by burning sulphur or pyrites in air is washed with water and the sulphur dioxide expelled from the solution by heating : the dry gas is then liquefied by compression. Liquid sulphur dioxide is sold in glass siphons or in steel containers. Sulphur dioxide is used in bleaching wool or straw, as a disinfectant, in making sulphites for the paper industry, and in making sulphuric acid. Liquid sulphur dioxide has been used in purifying petroleum products.

Properties.—Sulphur dioxide is a colourless gas $2\frac{1}{4}$ times as heavy as air (normal density 2.9267 gm./lit.), with a suffocating smell well known as that of burning sulphur. It is easily liquefied by compression ($2\frac{1}{2}$ atm. at 15°) or cooling to form a colourless liquid, b. pt. -10° , sp. gr. 1.434 at 0° , dielectric constant 13.75, critical temperature 157.15° , critical pressure 77.65 atm. The liquid dissolves iodine, sulphur, phosphorus, resins, and some salts. The salt solutions conduct the electric cur-

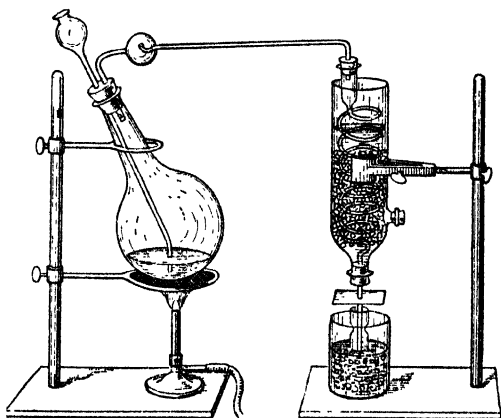


FIG. 259.—Liquefaction of SO_2 by cooling.

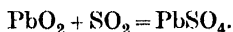
rent, so that the solvent has some ionising power. On rapid evaporation the liquid freezes to a snow-like solid, m. pt. -75.5° . Sulphur dioxide gas is decomposed in a strong beam of light, a cloud being formed (Morren, 1870) : $3\text{SO}_2 = 2\text{SO}_3 + \text{S}$.

The liquid is easily prepared by passing the gas into a glass spiral immersed in a mixture of pounded ice and salt (Fig. 259), and is collected in a strong tube with the neck drawn off, immersed in a freezing mixture. The neck may be sealed whilst the tube remains cooled.

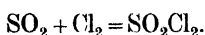
The gas does not support combustion in the ordinary sense, but heated potassium burns in it, forming potassium sulphite and thio-sulphate :



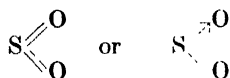
Finely divided tin and iron burn in the gas when heated, forming mixtures of oxides and sulphides. Pure lead dioxide heated in a bulb tube becomes incandescent when sulphur dioxide is passed over it and forms white lead sulphate :



Sulphur dioxide combines in sunlight with chlorine forming sulphuryl chloride, a volatile fuming liquid, easily hydrolysed by water (p. 484) :



The structural formula of sulphur dioxide is :

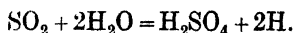


the molecule being bent (angle $O-S-O = 120^\circ$).

Sulphurous acid.—Sulphur dioxide is freely soluble in water (45 vols. to 1 of water at 15° ; 1 vol. of glacial acetic acid dissolves 318 vols. of sulphur dioxide at 15°) forming an acid liquid smelling strongly of the gas. This probably contains the unstable sulphurous acid H_2SO_3 , which has never been isolated. On boiling all the sulphur dioxide is evolved. When the saturated solution is strongly cooled crystals of the hydrate $SO_2 \cdot 6H_2O$ separate. The solution when heated in a sealed tube at 150° deposits sulphur :

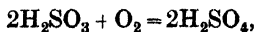


The solution has bleaching properties ; moistened wool, straw for hats, and other materials injured by chlorine are bleached on exposure to sulphur dioxide or the fumes of burning sulphur. This property (mentioned by Pliny) has been explained by two theories : (i) the formation of colourless addition compounds of sulphur dioxide with the colouring matters, or (ii) the reduction of the colours to colourless compounds, possibly by nascent hydrogen :



A dilute fuchsine ("magenta") solution is bleached by sulphur dioxide, but on boiling the colour is restored. Red roses may be bleached by wetting them and suspending in a bell-jar over burning sulphur ; on dipping the flowers into dilute sulphuric acid the colour is restored.

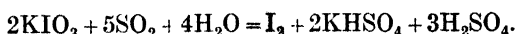
Sulphurous acid solution is slowly oxidised by atmospheric oxygen to sulphuric acid :



but the rate of oxidation is much reduced by adding glycerol, phenol, mannitol, benzaldehyde, or (especially) stannous chloride.

Titoff (1903) concluded that in perfectly pure water no oxidation would occur; oxidation is due to traces of iron and copper salts in all water, which act as catalysts. Even 1 gm. atom of Cu^{++} in 10^{12} ml. exerts an appreciable influence. Organic substances may form complex compounds with the metal ions; their action as negative catalysts may consist in their capability of destroying the positive catalysts (Cu^{++} , etc.). Another explanation is that negative catalysts break the "chains" of molecules produced by activation in a reaction (p. 216).

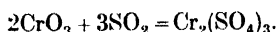
Sulphurous acid and sulphites are *reducing agents*; they liberate iodine from iodic acid or an iodate:



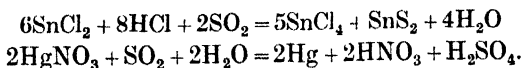
The titration of the liberated iodine is a means of estimation of SO_2 in flue-gases or sulphites in solution. With excess of sulphur dioxide the iodine is reduced: $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = 2\text{HI} + \text{H}_2\text{SO}_4$.

Sulphur dioxide decolorises a neutral solution of potassium permanganate: $2\text{KMnO}_4 + 5\text{SO}_2 + 2\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 2\text{H}_2\text{SO}_4$.

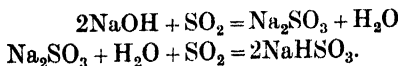
A piece of paper dipped in acidified potassium dichromate solution (yellow) becomes green in sulphur dioxide:



Sulphurous acid solution evolves hydrogen with magnesium. Sulphur dioxide and sulphites are reduced to hydrogen sulphide by zinc and hydrochloric acid; they precipitate *stannic* sulphide from a solution of *stannous* chloride in hydrochloric acid, and mercury from a solution of mercurous nitrate:

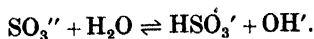


Sulphites.—Sulphurous acid is dibasic and forms two series of salts, which theoretically would have the formulae MHSO_3 and M_2SO_3 :

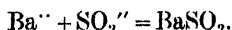


Divide a solution of sodium hydroxide into two equal parts. Saturate one with SO_2 producing a solution of **sodium hydrogen sulphite** NaHSO_3 . This is acid owing to the reaction: $\text{HSO}_3' \rightleftharpoons \text{SO}_3'' + \text{H}'$. Mix this with the other half of the alkali and evaporate. Crystals of normal **sodium sulphite** $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ separate on cooling.

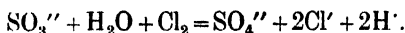
Sodium sulphite forms a slightly alkaline solution owing to hydrolysis:



Solutions of sulphites give a white precipitate of barium sulphite, *soluble in hydrochloric acid*, on addition of barium chloride :



If chlorine- or bromine-water is added, a white precipitate of barium sulphate, *insoluble in hydrochloric acid*, is formed :

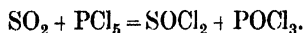


If a solution of sodium hydrogen sulphite is evaporated with excess of sulphur dioxide, or if sulphur dioxide is passed over crystals of sodium carbonate monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the solid sodium disulphite (*pyrosulphite or metabisulphite*) $\text{Na}_2\text{S}_2\text{O}_5$ (*i.e.* $\text{Na}_2\text{O} \cdot 2\text{SO}_2$), used in photography, is formed. On heating dry sodium sulphite the sulphate and sulphide are formed :



The disulphite on heating first decomposes into Na_2SO_3 and SO_2 , and the Na_2SO_3 then decomposes as above. The simple acid sulphites *e.g.* NaHSO_3 do not appear to exist in a solid form : the commercial solid "bisulphite" is probably mostly $\text{Na}_2\text{S}_2\text{O}_5$. The sulphites of calcium $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$, strontium SrSO_3 , and silver Ag_2SO_3 are white and insoluble ; cuprous sulphite Cu_2SO_3 is red and insoluble. Magnesium, zinc and cadmium sulphites, $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_3 \cdot 5\text{H}_2\text{O}$, and $\text{CdSO}_3 \cdot \text{H}_2\text{O}$ are white and sparingly soluble.

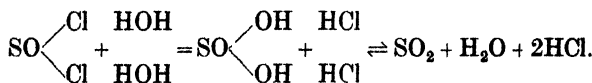
Thionyl chloride.—If sulphur dioxide is passed over phosphorus pentachloride, a liquid is formed which on fractional distillation is separated into thionyl chloride SOCl_2 (b. pt. 78°) and phosphorus oxychloride POCl_3 (b. pt. 107°) :



Thionyl chloride is also formed by the addition of sulphur to chlorine monoxide at -12° : $\text{Cl}_2\text{O} + \text{S} = \text{SOCl}_2$. It is manufactured by adding sulphur trioxide to sulphur chloride at 75° - 80° , and passing a stream of chlorine into the mixture to reconvert the separated sulphur into sulphur chloride :



Thionyl chloride is the chloride of the bivalent *thionyl* radical, $-\text{SO}-$. It is a colourless liquid, sp. gr. 1.677 at 0° , which fumes in moist air and is decomposed by water, forming hydrochloric and sulphurous acids ; it is an acid chloride, *i.e.* sulphurous acid with univalent hydroxyl replaced by chlorine :



A general method of preparation of an acid chloride is by the action of phosphorous pentachloride on the acid, when the acid chloride,

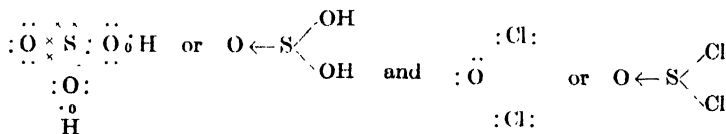
phosphorus oxychloride (POCl_3) and hydrogen chloride are formed. In the present case the acid anhydride (sulphur dioxide) is used, and hydrogen chloride is not formed.

Thionyl bromide SOBr_2 , a red liquid, b. pt. $59^\circ/40$ mm., is formed by acting on SOCl_2 with gaseous HBr : $\text{SOCl}_2 + 2\text{HBr} = \text{SOBr}_2 + 2\text{HCl}$. Thionyl chlorobromide SOClBr was said by Besson also to be produced in this reaction, but Mayes and Partington (1926) were unable to confirm this. Thionyl fluoride SOF_2 is a colourless gas obtained by heating SOCl_2 and arsenic fluoride AsF_3 : $2\text{AsF}_3 + 3\text{SOCl}_2 = 2\text{AsCl}_3 + 3\text{SOF}_2$. It boils at -32° . Gaseous thionyl chlorofluoride SOClF is formed from SOCl_2 , SbF_3 and SbCl_5 .

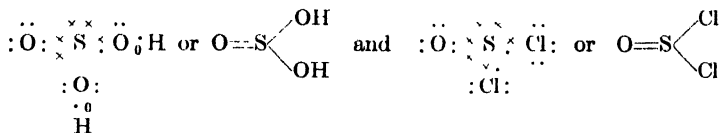
The constitution of sulphurous acid.—The formation of sulphurous acid by the action of water on thionyl chloride suggests that it has the symmetrical formula HO.SO.OH . By the action of thionyl chloride on alcohol symmetrical diethyl sulphite EtO.SO.OEt , b. pt. 161° , is formed.

By the oxidation of mercaptan EtSH with dilute nitric acid ethylsulphonic acid EtSO_3H , is formed, the ethyl ester of which, EtSO_3Et , is obtained by the action of sodium sulphite on ethyl iodide. In the sulphonic acid the ethyl group is directly attached to sulphur, as in mercaptan. Sulphurous acid, therefore, behaves as if it had two formulae, the symmetrical HO.SO.OH , and the unsymmetrical $\text{H.SO}_2.\text{OH}$ (sulphonic acid).

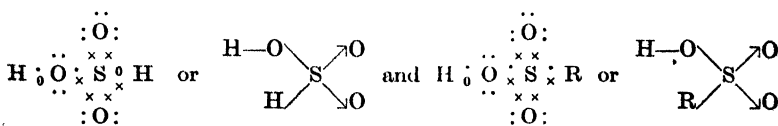
The *symmetrical* formulae of sulphurous acid and thionyl chloride may be written as :



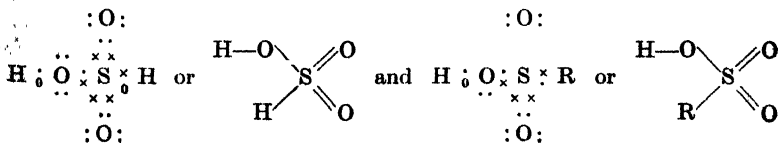
or (more probably) with 4-valent sulphur :



The *unsymmetrical* formulae for sulphurous acid and a sulphonic acid ($\text{R} = \text{Et}$, etc.) may be written :



or (more probably) with 6-valent sulphur :

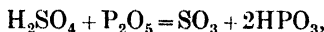


If the $[O_2]$ concentration is increased, the $[SO_3]$ concentration must increase and maintain K constant.

Other catalysts such as ferric oxide and vanadium pentoxide can be used instead of platinum, but the temperature must then be higher, and since the reaction $2SO_2 + O_2 = 2SO_3$ is exothermic, Le Chatelier's principle (p. 295) shows that the equilibrium yield of SO_3 must be smaller at higher temperatures. At lower temperatures the reaction is too slow.

At 450° , 2 per cent of pure SO_3 is decomposed, at 700° , 40 per cent. In a mixture of SO_2 and air, obtained by burning pyrites, containing by volume 7 per cent of SO_2 , 10.4 per cent of O_2 , and 82.6 per cent of N_2 , the percentages of SO_2 oxidised to SO_3 in equilibrium are: at 434° , 99; at 550° , 85; at 645° , 60. The change $2SO_2 + O_2 = 2SO_3 + 45$ k. cal., does not proceed in presence of platinum at an appreciable rate below 400° , on account of the slowness of reaction at lower temperatures. The two conflicting effects of temperature on the yield are balanced in practice by working at 400° – 450° , which is the *optimum* temperature with platinum as a catalyst, and using excess of oxygen in the form of air.

Sulphur trioxide is produced by heating concentrated sulphuric acid with a large excess of phosphorus pentoxide:

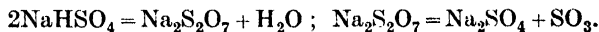


or most conveniently on the small scale by distilling fuming sulphuric acid in a retort and collecting the sulphur trioxide in a perfectly dry receiver cooled in a freezing mixture:

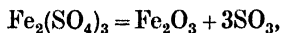


Sulphur trioxide was first made in this way by Bernhardt in 1755.

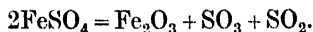
Sodium hydrogen sulphate at 300° forms sodium disulphate and this evolves sulphur trioxide at a bright-red heat:



Sulphur trioxide is evolved on heating ferric sulphate:



or dry ferrous sulphate:



Sulphur trioxide exists in more than one modification. The liquid, b. pt. 44.52° , first formed in the cooled tube solidifies on cooling to transparent crystals, m. pt. 16.85° , sp. gr. 1.9255 at 20° , called α - SO_3 ; these on standing (at least in presence of a trace of moisture) soon form silky asbestos-like crystals of β - SO_3 , and there may be two forms of this, m. pts. 32.5° and 62.2° . At 50° β - SO_3 slowly changes into α - SO_3 .

The vapour density of sulphur trioxide corresponds with the formula SO_3 . When passed through a red-hot tube the vapour is decomposed, giving 2 vols. of SO_2 and 1 vol. of O_2 which do not recombine on cooling

in the absence of a catalyst: $2\text{SO}_3 = 2\text{SO}_2 + \text{O}_2$. In this way the composition and formula may be found. The solid absorbs moisture from the air with avidity, giving off dense white fumes of droplets of sulphuric acid: $\text{H}_2\text{O} + \text{SO}_3 = \text{H}_2\text{SO}_4$. It dissolves in water with a loud hissing noise and great evolution of heat, but dissolves readily and quietly in concentrated sulphuric acid; the *fuming sulphuric acid* so obtained solidifies on cooling to colourless crystals of disulphuric acid $\text{H}_2\text{S}_2\text{O}_7$, m. pt. 35° . Sulphur trioxide reacts violently with baryta, the mass becoming incandescent: $\text{SO}_3 + \text{BaO} = \text{BaSO}_4$.

The contact process.—Sulphuric acid and fuming sulphuric acid are made by the so-called "contact" process, in which sulphur dioxide and oxygen (in the form of air) combine to form sulphur trioxide in presence of a catalyst. The apparatus is very compact as compared with the lead chamber plant. When platinum is used as a catalyst the gases must be carefully purified, since otherwise the platinum loses its activity or is "poisoned". Arsenious oxide, sulphuric acid fog, and dust in the gases from pyrites burners are removed by introducing steam and cooling, then filtering the gas through coke wetted with concentrated sulphuric acid until no fog is seen in a powerful beam of light ("optically clear" gas).

In the **Badische process** the purified gas is passed through an iron converter (Fig. 261) with vertical iron tubes packed with platinised

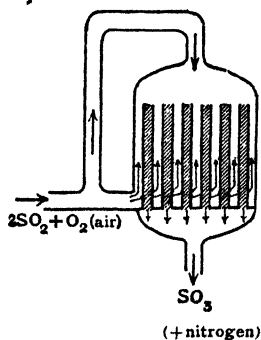


FIG. 261.—Badische converter.

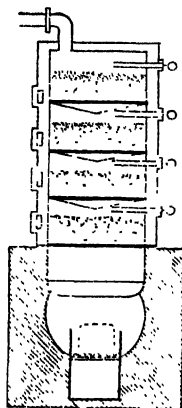


FIG. 262.—Schröder-Grillo converter.

asbestos. Twice the theoretical amount of oxygen (in the form of air) is present in the gas, which is pre-heated to start the reaction. By letting part of the incoming gas sweep over the outside of the hot tubes in which reaction occurs no external heating is needed, since heat is evolved and the process goes on continuously. In modern plants a

preparation of vanadium pentoxide supported on silica granules, or platinised silica gel, are used as catalysts; they are immune to arsenic poisoning.

In the Schröder-Grillo process the catalyst is prepared by moistening Epsom salt $MgSO_4 \cdot 7H_2O$ with a solution of platinum chloride and heating in presence of sulphur dioxide. The salt loses water and swells up to a voluminous contact mass on which the platinum is very finely divided. This is put on shelves in iron converters, lagged outside (Fig. 262), and when the process is started it goes on without external heating.

The Mannheim process utilises burnt pyrites (Fe_2O_3 and a little CuO) as the contact mass. This is filled into a rectangular tower, the lower part of which communicates with four pyrites burners arranged in a +, to which air dried in a sulphuric acid tower is supplied (Fig. 263). The hot gases pass directly to the iron oxide shaft, and on account of the higher temperature only about 60 per cent of the SO_2 is converted into SO_3 . The arsenious oxide in the burner gases is kept back in the oxide of iron as ferric arsenate, and after the SO_3 has been absorbed from the exit gas by sulphuric acid, the gas is filtered

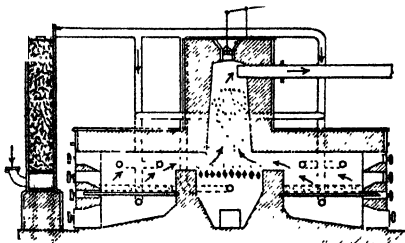


Fig. 263.—Mannheim contact process.

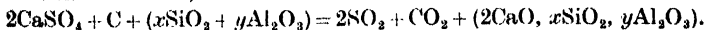
through scrubbers of coke soaked in concentrated sulphuric acid, reheated, and passed to a Tenteleff converter to finish the conversion.

The Tenteleff process utilises a catalyst composed of asbestos "sponge-cloths" which are platinised by being soaked in platinic chloride solution and the latter reduced by formaldehyde. These are superimposed in an iron frame, 3 ft. by 2 ft., interposed in the gas current. The temperature is 450° – 500° .

The sulphur trioxide cannot be absorbed from a converter gas by passing through water, as a dense fog of minute droplets of H_2SO_4 is thus formed, which cannot be condensed. The gas is therefore passed into 97–99 per cent sulphuric acid in iron towers; the concentrated acid rapidly absorbs the SO_3 , producing fuming sulphuric acid or *oleum*; or if a regulated stream of water is admitted, the 97–99 per cent acid is continuously increased in quantity by the reaction $SO_3 + H_2O = H_2SO_4$ occurring in the liquid acid.

With a vanadium pentoxide catalyst, the main part of the conversion is carried out at a higher temperature, but in the gas passing to the upper part of the catalyst mass, where the temperature is lower, the remaining sulphur dioxide is converted into trioxide.

In some plants the sulphur dioxide is produced by heating a mixture of native calcium sulphate, coal, and coal ash (containing silica and alumina) in a cement furnace, in which cement clinker is formed:



The gas is purified and dried; the presence of carbon dioxide does not interfere with the conversion of SO_2 into SO_3 .

Fuming sulphuric acid is an oily liquid, often coloured brown by organic matter but colourless when pure, which emits thick white fumes in moist air. It may be kept in mild steel drums, but cracks cast iron (which resists the action of ordinary concentrated sulphuric acid). It is made with different contents of free SO_3 , i.e. SO_3 in excess of the amount required to form H_2SO_4 . The strongest product contains 60 per cent of free SO_3 , and emits very dense fumes.

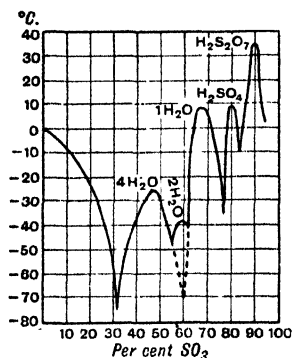


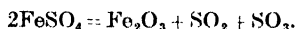
FIG. 264.—The system sulphur trioxide-water.

The hydrates $\text{H}_2\text{O}, \text{SO}_3$ (H_2SO_4 , or *monohydrate*, m. pt. 10.49°); $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ or $\text{SO}_3, 2\text{H}_2\text{O}$ (m. pt. 8.62°); $\text{H}_2\text{O}, 2\text{SO}_3$ or $\text{H}_2\text{S}_2\text{O}_7$ (*disulphuric acid*, m. pt. 35°); $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ (m. pt. -38.9°), and $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ (m. pt. -29°) are known. Acids containing more than 60 and less than 40 per cent of free SO_3 are liquid at the ordinary temperature, the others are solid. Oleum may be added to ordinary sulphuric acid to increase its concentration.

The four hydrates of SO_3 , viz. $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, H_2SO_4 , and $\text{H}_2\text{S}_2\text{O}_7$, are shown as maxima on the freezing-point curve (Fig. 264).

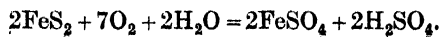
SULPHURIC ACID

History.—Sulphuric acid or *oil of vitriol* was obtained by the alchemists by distilling *green vitriol* (ferrous sulphate) :



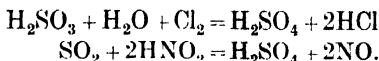
In 1666 Le Févre obtained the acid by burning sulphur in presence of moisture; Lemery in 1675 made it by burning a mixture of sulphur and nitre over a dish of water under a glass bell, and a small works using this process was established in 1740 by Ward at Richmond. The acid obtained was called *oil of vitriol per campanam*. Roebuck in 1746 in Birmingham, and in 1749 at Prestonpans, replaced the fragile glass vessels by lead chambers 6 ft. wide, and these were enlarged in later works. A continuous process in which the sulphur dioxide was produced from sulphur in separate burners and admitted with nitrous fumes, air, and steam to the chambers was introduced by Holker into the French works of Chaptal in 1810. The use of pyrites and the invention of the Gay-Lussac (1827) and Glover (1859) towers led to the modern industry. The chamber process has been considerably improved and is still very largely used for making ordinary (not fuming) sulphuric acid.

Occurrence.—Free sulphuric acid occurs in traces in rain water of towns where coal (containing sulphur compounds) is burnt, and in some rivers and springs which have been in contact with beds of pyrites :

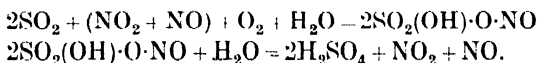


In combination as sulphates it forms common minerals, *e.g.* $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4 , and PbSO_4 .

Preparation.—Sulphuric acid is formed from sulphur trioxide and water: $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$. Moist flowers of sulphur exposed to air slowly oxidise to sulphuric acid. Sulphurous acid solution oxidises slowly when exposed to air: $2\text{H}_2\text{SO}_3 + \text{O}_2 = 2\text{H}_2\text{SO}_4$. Oxidation is more rapid when hydrogen peroxide is shaken in a jar of sulphur dioxide: $\text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4$, or when chlorine water, bromine water or nitrous acid is added:

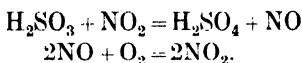


The lead chamber process.—Sulphuric acid is manufactured by the lead chamber process. The reactions in the lead chamber occur between sulphur dioxide, oxygen (air), steam (or water-spray), and oxides of nitrogen ("nitrous fumes"). Clement and Desormes in 1806 discovered an intermediate compound in the reaction, *viz.* nitrososulphuric acid ("chamber crystals"), *i.e.* sulphuric acid $\text{HO}\cdot\text{SO}_2\cdot\text{OH}$ in which one H is replaced by the nitroso-group NO, giving $\text{HO}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}$. It may be formed and decomposed alternately in the chambers:

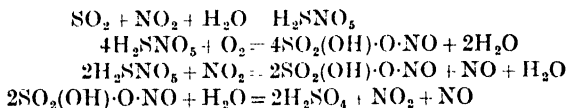


The nitrous gas or mixture $\text{NO}_2 + \text{NO}$ therefore acts in a cyclic manner as a catalyst.

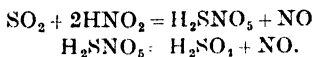
A simpler explanation assumes that sulphurous acid* is oxidised to sulphuric acid by nitrogen dioxide, and the nitric oxide formed is then reoxidised by atmospheric oxygen:



Lunge and Berl (1906) assumed the formation of a hypothetical acid H_2SNO_5 (p. 561):



Raschig (1887) supposed that H_2SNO_5 is formed by the action of nitrous acid:



The lead chamber reactions may be illustrated by the following experiment.

* Sulphur dioxide in absence of water is not oxidised to sulphur trioxide by NO_2 but undergoes a different reaction; according to Michaelis (1874) and Manchot (1929) nitrosyl disulphate $(\text{NO})_2\text{S}_2\text{O}_7$ is formed.

A dry 6-litre flask *A* (Fig. 265) is fitted with tubes as shown. Three of the tubes are connected with wash-bottles containing concentrated sulphuric acid. One of these is connected with a siphon of liquid SO_2 , one to a gas-holder containing oxygen, the third to a gas-holder containing nitric oxide, and the fourth with a small flask *B* containing water which may be heated, and through which oxygen may be bubbled. A stream of dry oxygen is first passed through *A*. Nitric oxide is then passed in and forms red

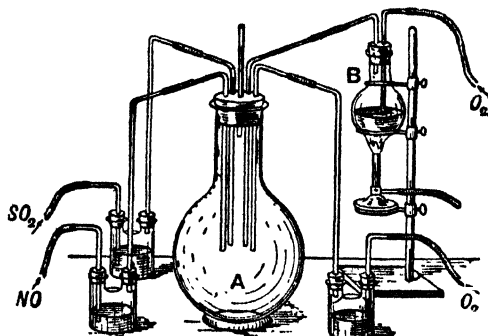


FIG. 265.—Experiment illustrating the chamber process.

high oxides of nitrogen. Sulphur dioxide is then passed in at the same rate as the nitric oxide and after a short time a current of oxygen is passed through the hot water in *B* to carry moisture into the globe. Colourless star-shaped crystals of nitroso-sulphuric acid form on the inside of the globe and the colour of the gas becomes paler. The gas is swept out by a rapid current of oxygen and the water in *B* is boiled. When the steam comes in contact with the crystals they dissolve with effervescence, producing red oxides of nitrogen and fairly concentrated sulphuric runs down to the bottom of the flask. If insufficient water is used in the first stage, a white powdery deposit is formed which gives purple drops in contact with steam.

On the large scale (Fig. 266) iron pyrites is burnt in brick furnaces called pyrites burners, the grates of which are composed of separate

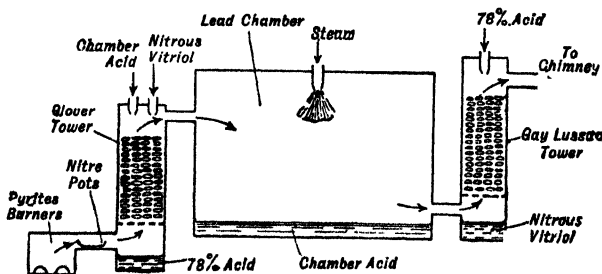


FIG. 266.—Sulphuric acid chamber plant (diagrammatic).

square bars which can be turned on their longitudinal axes so as to drop the burnt ore into the ashpits. The supply of air is carefully regulated by sliding doors above and below the bed of pyrites. Each furnace holds 3–5 tons of ore, and they are arranged in sets of 20–25, with a communicating flue for each set of chambers. The daily charge for each

furnace is 750–1000 lb. of pyrites. Pyrites powder or “spent oxide” (p. 450) is burnt in kilns consisting of iron cylinders lined with firebrick, with a series of shelves so arranged that the ore is raked from shelf to shelf until the burnt ore is discharged at the bottom. The rakes are actuated by a revolving air- or water-cooled central shaft. Sulphur is burnt in large inclined rotating cylinders or other type of special burner.

The burner gas (7 per cent of SO_2 , 10 per cent of O_2 , 83 per cent of N_2) passes to a dust-catcher containing baffle-walls, and then through a nitre-oven in which pots containing sodium nitrate and sulphuric acid are placed. These supply the oxides of nitrogen to make up losses from the plant. About 3 parts of NaNO_3 per 100 parts of sulphur burnt as pyrites are used. In modern plants, the oxides of nitrogen are supplied by the oxidation of ammonia (p. 540).

From the nitre-oven the hot gases at 300° – 400° pass into the Glover tower, a squat lead tower 20 to 30 ft. high and 6 to 8 ft. diameter lined with acid-resisting bricks and packed with flints resting on an arch. Down this tower two streams of acid pass from tanks at the top, one of acid (65 to 70 per cent H_2SO_4) from the lead chambers and the other of stronger acid (78 per cent H_2SO_4) containing oxides of nitrogen (in the form of nitrososulphuric acid) from the Gay-Lussac tower. The functions of the Glover tower are: (a) to cool the burner gases to 50° – 80° before they enter the chambers; (b) to denitrate the acid from the Gay-Lussac tower by dilution with chamber acid and heating, and by reaction with sulphur dioxide; (c) to concentrate the chamber acid to about 78 per cent H_2SO_4 for sale or for use in the Gay-Lussac tower, and at the same time provide part of the steam for the chambers. About 25 per cent of the total acid made is formed by reactions in the Glover tower.

From the Glover tower the gases pass by a lead main to the set of three or more large lead chambers, constructed of sheet lead weighing 6–8 lb. per sq. ft. The chambers are oblong or square in shape and dip into large lead trays with a seal of acid. They are suspended from a wooden or iron frame by lead straps on the sides. All joints in the lead sheets are autogenously welded by a hydrogen flame. The capacity of each chamber is 25,000–75,000 cu. ft. and they are connected by wide lead pipes. Drum-shaped or polygonal (“Mills-Packard”) chambers sometimes cooled by water flowing over the outside, or even packed towers, are used in some modern plants, but adequate empty space is necessary for the reoxidation of NO , which is rather slow and hence towers are often combined with chambers.

Steam or more usually a fine spray of liquid water from several jets in the roof is blown into the chamber. Sulphuric acid is produced in the form of a fog of small drops which settle down as liquid chamber acid (65–70 per cent H_2SO_4) on the floor of the chamber.

The gases from the last chamber contain nitrogen, a little oxygen, most of the oxides of nitrogen in circulation through the plant, and a trace of sulphur dioxide. They pass to the Gay-Lussac tower, a lined lead tower 40 to 60 ft. high and 8 to 15 ft. diameter, packed with hard coke or pieces of flint and fed with cold Glover tower acid (78 per cent H_2SO_4). Its function is to recover the oxides of nitrogen in the exit gases from the chambers. These are absorbed producing nitrous nitriol

containing nitrosulphuric acid equivalent to 1 to 2 per cent of N_2O_3 , which is pumped to the Glover tower for denitration. The waste gas from the Gay-Lussac tower passes to a chimney or fan which maintains a draught through the whole system. In modern practice a high concentration of oxides of nitrogen ("circulating nitre") with adequate absorption capacity in the Gay-Lussac towers is used, and the reaction proceeds rapidly but with greater wear of the lead chambers. The conversion of SO_2 to H_2SO_4 reaches 98 per cent.

Concentration of sulphuric acid.—The acid from the Glover tower contains about 78 per cent of H_2SO_4 . It is generally dark coloured from contact with organic matter and is called "brown oil of vitriol" (B.O.V.). It is sufficiently concentrated for some commercial purposes, e.g. for making superphosphate of lime or saltcake, but for others it must be further concentrated to form "rectified oil of vitriol" (R.O.V.) con-

taining 93 to 95 per cent of H_2SO_4 . This concentration was formerly carried out by heating the acid in glass or platinum retorts, when vapours of weak acid come off and more concentrated acid remains. The concentration is now carried out in special apparatus.

A simple type is the **cascade process**, in which the acid is allowed to flow down a series of silica or ferro-silicon dishes arranged one above the other with the spout of one discharging into the basin next lower, the whole resting on a kind of staircase of acid-resisting bricks. The acid is heated by a flue below and hot air sweeps over its surface. From the last dish, which may be of cast iron, the acid flows to a cooler.

In the **Kessler apparatus** the acid flows through a dish *S* of Volvic stone (a natural acid-resisting material of volcanic origin, found at Puy-de-Dôme) covered outside with lead, through which hot gas from a coke furnace passes (Fig. 267). The dish has ridges *b* so as to bring the acid and fire-gas into intimate contact. The concentrated acid runs off to a cooler.

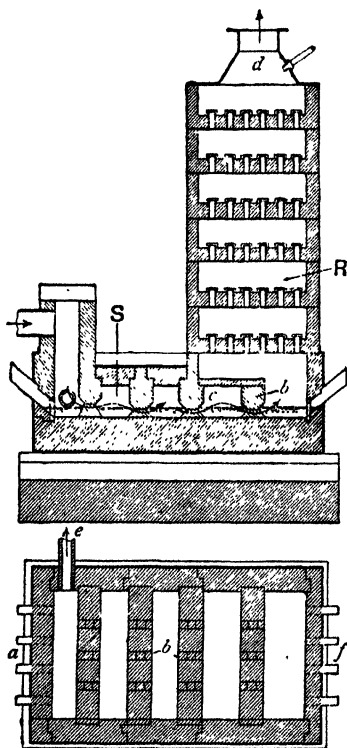


FIG. 267.—Kessler apparatus for concentrating sulphuric acid.

The fumes pass through a tower *R* containing a number of plates with perforations covered with inverted cups, down which the acid to be concentrated is fed. Much of the fume is here condensed, and the temperature is

kept at such a point that steam escapes but the sulphuric acid remains. The issuing fumes then pass through a lead box packed with graded coke drenched with concentrated sulphuric acid, which takes out the fine mist of acid droplets. In America, hot gases from a burning spray of petroleum are bubbled through the acid.

The Gaillard tower (Fig. 268) consists of an empty tower of Volvic stone or acid-resisting brick, from the top of which a fine spray of acid is discharged. In passing down the tower this spray meets a current of hot gas from a coke furnace, which enters the tower at the side near the bottom. The acid fumes pass through a smaller empty lead tower called a recuperator, down which part of the acid to be concentrated is sprayed, and then to coke filters drenched with concentrated sulphuric acid. The concentrated acid runs out to a cooler from a lead tray in which the tower stands.

The acid fumes from concentrators may be condensed by means of electrostatic precipitation. They are passed through a chamber in which lead plates are hung, with lead covered bars hanging vertically between them. These are charged to a potential of 20,000 volts. The acid droplets are attracted to the plates and the liquid deposited on the latter runs off to collecting tanks to be returned to the concentrators.

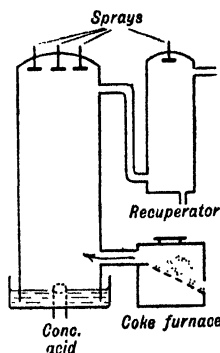


FIG. 268. —Gaillard tower.

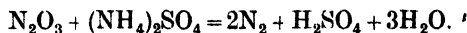
More concentrated acid (97-98 per cent of H_2SO_4) is made by heating 93-95 per cent acid in pans by direct fire. The strongest acid does not attack cast-iron, whilst 93-95 per cent acid dissolves it. The acid is run in a thin stream on to the surface of a large bulk of 98 per cent acid, boiling in a large cast-iron pot provided with a siphon neck opening into it near the bottom. The strong acid is run off continuously from this "swan-neck" as concentration proceeds. The acid may also be brought to any desired strength by the addition of oleum (sulphuric acid containing free SO_3).

(Most of the sulphuric acid is used (as chamber acid) for superphosphate manufacture; next important is the use of concentrated acid for petroleum refining. The rest is used for chemicals, refining coal products, in metallurgical processes, making artificial silk and explosives (when fuming acid is often used), in storage batteries, etc. Some processes which formerly used sulphuric acid (*e.g.* making nitric and hydrochloric acids) are now often carried on without it.)

The purification of sulphuric acid.—Commercial sulphuric acid often contains arsenic trioxide As_2O_3 in solution, derived from the arsenic in the pyrites. It is purified with hydrogen sulphide in lead towers or closed agitators. The precipitate of arsenic sulphide As_2S_3 is filtered by suction through unglazed earthenware plates, or is removed by flotation; a little paraffin added to the liquid floats to the surface and carries the precipitate with it. Acid made from sulphur ("brimstone acid") is preferred for the preparation of foods and for lead accumulators (in

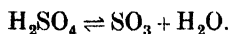
which acid free from iron salts is essential), although purified acid from pyrites is also used.

Oxides of nitrogen may be removed by strongly heating with a small quantity of ammonium sulphate :



The commercial acid usually contains lead sulphate, most of which is deposited on dilution with water.

Properties of sulphuric acid.—Pure sulphuric acid (*monohydrate*) is prepared by adding the requisite amount of SO_3 to 98 per cent acid. It is an oily liquid which fumes slightly in air, from dissociation in the liquid :



This dissociation increases on heating and the vapour is richer in SO_3 than the liquid. It is therefore impossible to obtain the pure acid by the ordinary concentration process. On boiling, an acid of constant composition (98.3 per cent H_2SO_4) comes over at a temperature of 338° , which is usually given as the boiling point of sulphuric acid. The 95 per cent acid boils at 295° . The ordinary acid (98 per cent H_2SO_4) is a colourless oily liquid of density 1.84, which does not fume.

Concentrated sulphuric acid is very corrosive and has a strong affinity for water ; when mixed with water much heat is given out and the liquid may boil ; the acid should always be added to the water in a thin stream with stirring, never the water to the acid. The diluted acid occupies a smaller volume than its constituents and the contraction is a maximum for $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$. If the acid is mixed with snow, cold is produced, as the latent heat of fusion of ice exceeds the evolution of heat on mixing the acid with liquid water.

The large evolution of heat and the contraction on mixing sulphuric acid and water point to a chemical change and many properties show maximum or minimum values at *approximately* whole molecular ratios of acid and water. This has been taken to imply definite hydrates in the *liquid state*, but the maxima and minima occur at different values for different properties : contraction (maximum, $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$), viscosity (max. $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ and $\text{H}_2\text{S}_2\text{O}_7$; min. $3\text{H}_2\text{SO}_4, \text{H}_2\text{O}$), surface tension (max. $\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$), compressibility (min. $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$), index of refraction (max. $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$), electrical conductivity (max. $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$), and heat of solution (max. $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$).

The density of pure sulphuric acid at 15° is 1.8384, those of mixtures of the acid and water at 15° and of fuming sulphuric acid ("oleum") containing free sulphur trioxide are given in the table. The 97.7 per cent acid has a maximum density of 1.8414, and the density of oleum is a maximum for 60 per cent of free SO_3 .

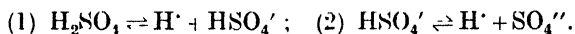
SULPHURIC ACID				OLEUM	
H ₂ SO ₄ p.c.	Density	H ₂ SO ₄ p.c.	Density	Free SO ₃ p.c.	Density
1.0	1.0061	60	1.5024	10	1.888
5	1.0332	65	1.5578	20	1.920
10	1.0681	70	1.6151	30	1.957
15	1.1045	75	1.6740	40	1.979
20	1.1424	80	1.7324	50	2.009
25	1.1816	85	1.7841	60	2.020
30	1.2220	90	1.8198	70	2.018
35	1.2636	95	1.8388	80	2.008
40	1.3065	97	1.8414	90	1.990
45	1.3514	98	1.8411	100	1.984
50	1.3990	99	1.8393		
55	1.4494	100	1.8384		

Concentrated sulphuric acid chars organic matter, removing the elements of water and leaving black carbon.

To strong sugar syrup in a beaker standing in a stoneware trough add concentrated sulphuric acid and stir. The mixture becomes dark and froths to a black mass of carbon, steam and sulphur dioxide being evolved.

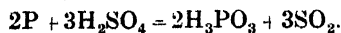
The vapour density of sulphuric acid at 444° corresponds with almost complete dissociation: $\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}$, but the products recombine on cooling. When the acid is heated in an open flask the steam diffuses more rapidly and the liquid is enriched in SO_3 (Wanklyn and Robinson, 1863). If the acid vapour is passed through a strongly heated platinum or quartz tube it decomposes into oxygen, sulphur dioxide and steam, which do not recombine on cooling: $2\text{H}_2\text{SO}_4 = 2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$. This also occurs if the acid is dropped into a red-hot platinum flask.

Sulphuric acid ionises in two stages, the first nearly complete but the second appreciable only at high dilution:



The acid and normal sulphates are MHSO_4 and M_2SO_4 (M univalent), but disulphates $\text{M}_2\text{S}_2\text{O}_7$ and more complex sulphates, formed from normal sulphates and sulphur trioxide, $\text{M}_2\text{SO}_4 \cdot x\text{SO}_3$, are known. Many normal sulphates occur as minerals: gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrite CaSO_4 , celestine SrSO_4 , barytes BaSO_4 , glauberite $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$, and kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ are some examples. Many sulphates are soluble and crystalline, but calcium, strontium and lead sulphates are sparingly soluble, and barium sulphate is almost insoluble in water and dilute acids.

Sulphuric acid is only very slowly reduced by hydrogen in the cold (not appreciably at 0°) but more rapidly on heating: $\text{H}_2\text{SO}_4 + \text{H}_2 = \text{SO}_2 + 2\text{H}_2\text{O}$. Carbon, sulphur, and phosphorus reduce the hot acid:



Its vapour at 170°–180° is decomposed into sulphuryl chloride and sulphuric acid : $2\text{SO}_3\text{HCl} = \text{SO}_2\text{Cl}_2 + \text{H}_2\text{SO}_4$, and at higher temperatures into chlorine, sulphur dioxide and steam. It reacts violently with silver nitrate, forming nitrososulphuric acid :



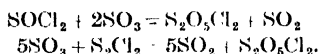
A sodium salt is formed by the action of sodium chloride on the acid :



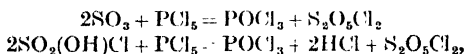
Sulphuryl chloride (Regnault, 1838) is formed by direct combination of sulphur dioxide and chlorine in sunlight or in presence of catalysts such as charcoal, camphor, or acetic anhydride : $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$. It is formed by heating chlorosulphonic acid in a sealed tube at 180°, or with a little mercuric sulphate, antimony, or tin as a catalyst, in a flask at 70° under a reflux condenser : $2\text{SO}_3\text{HCl} = \text{SO}_2\text{Cl}_2 + \text{H}_2\text{SO}_4$. It is a colourless fuming liquid, sp. gr. 1.667 at 20°, b. pt. 69.1° without decomposition ; the vapour is much dissociated at 330° : $\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$. The liquid is rather slowly hydrolysed by water : $\text{SO}_2\text{Cl}_2 + 2\text{H}_2\text{O} = \text{SO}_2(\text{OH})_2 + 2\text{HCl}$, and chlorosulphonic acid is formed as an intermediate stage : $\text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{SO}_2(\text{OH})\text{Cl} + \text{HCl}$.

With ice-cold water it forms a crystalline hydrate $\text{SO}_2\text{Cl}_2 \cdot 15\text{H}_2\text{O}$. A solution of sulphuryl chloride in petrol is used to make wool unshrinkable : it breaks some linkages in the spiral fibre molecules.

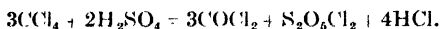
The chloride of disulphuric acid, disulphuryl chloride (or *pyrosulphuryl chloride*) $\text{S}_2\text{O}_5\text{Cl}_2$ is obtained by the action of sulphur trioxide on thionyl chloride or preferably on sulphur chloride (Rose, 1838) :



It is formed by the action of sulphur trioxide or chlorosulphonic acid on phosphorus pentachloride :

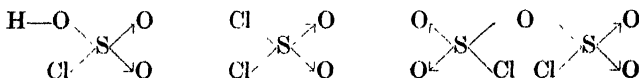


and by dropping fuming sulphuric acid into hot carbon tetrachloride :



It is a heavy mobile liquid, sp. gr. 1.844/18°, boiling at 57°/30 mm., or 150.7°/730 mm., giving a nearly normal vapour density, although some decomposition into sulphur dioxide, sulphur trioxide and chlorine occurs : $\text{S}_2\text{O}_5\text{Cl}_2 = \text{SO}_2 + \text{SO}_3 + \text{Cl}_2$. It fumes only slightly and is decomposed only slowly by water : $\text{S}_2\text{O}_5\text{Cl}_2 + 3\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + 2\text{HCl}$.

The conventional formulæ of the chlorides of sulphuric and disulphuric acids follow from those of the acids (see p. 483) :



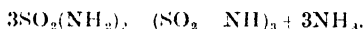
Fluosulphonic acid $\text{SO}_2(\text{OH})\text{F}$ is formed by distilling fluorspar with fuming sulphuric acid in an iron retort: $\text{SO}_3 + \text{HF} = \text{SO}_2(\text{OH})\text{F}$. It is a colourless mobile liquid, b.pt. 162.6° , the vapour being stable at 900° . The acid is incompletely hydrolysed by water: $\text{SO}_2(\text{OH})\text{F} + \text{H}_2\text{O} = \text{SO}_2(\text{OH})_2 + \text{HF}$, and very stable salts are formed from sulphur trioxide and alkali fluorides: $\text{SO}_3 + \text{NaF} = \text{SO}_2(\text{ONa})\text{F}$.

Sulphuryl fluoride SO_2F_2 is formed by passing heated fluorine into excess of sulphur dioxide: $\text{SO}_2 + \text{F}_2 = \text{SO}_2\text{F}_2$, or more conveniently by heating barium fluosulphonate: $\text{Ba}(\text{SO}_3\text{F})_2 = \text{BaSO}_4 + \text{SO}_2\text{F}_2$. It is a colourless stable inert gas, b.pt. -52° , m.pt. 120° , sparingly soluble in water. It is decomposed by sodium only at a high temperature, but is decomposed by alkali solution: $\text{SO}_2\text{F}_2 + 4\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{NaF} + 2\text{H}_2\text{O}$.

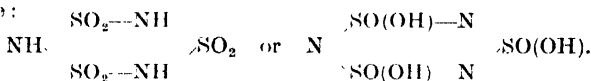
Sulphamide and sulphimide.—The action of ammonia gas on a solution of sulphuryl chloride in dry benzene forms *sulphamide* $\text{SO}_2(\text{NH}_2)_2$ (Regnault, 1838): $\text{SO}_2\text{Cl}_2 + 4\text{NH}_3 = \text{SO}_2(\text{NH}_2)_2 + 2\text{NH}_4\text{Cl}$.

It is purified by decomposing the silver compound $\text{SO}_2(\text{NHAg})_2$ with hydrochloric acid and forms large colourless crystals.

Sulphimide is polymerised, $(\text{SO}_2 \text{ NH})_3$: it is formed by heating sulphamide at 180° till ammonia is no longer evolved (Traube, 1892):



It is purified by decomposing the silver compound $(\text{SO}_2 \text{ NHAg})_3$ with hydrochloric acid, and forms colourless crystals. It probably has a ring structure:



Higher oxides of sulphur.—By the action of a silent discharge on a mixture of sulphur dioxide and oxygen Berthelot (1878) found a contraction, and a viscous liquid separated on the walls of the ozoniser, solidifying at 0° to long prismatic crystals, the analysis of which gave the formula S_2O_7 , *persulphuric anhydride*. These gave an oxidising solution of persulphuric acid with water. Meyer, Baillou and Henkel (1922) and Maisin (1928) found that the prolonged action of the discharge gave $\text{SO}_3, 2\text{SO}_4$, and Schwarz and Achenbach (1934) reported that with a glow discharge at low pressure and cooling the gas with liquid air, white solid *sulphur tetroxide* SO_4 separated, melting at 0° to oily drops of S_2O_7 .

Persulphuric acids.—Faraday (1834) when electrolysing a concentrated solution of sulphuric acid noticed "a remarkable disappearance of oxygen." He thought this was due to the formation of hydrogen peroxide, but this was not found by Brodie (1864), who suggested that persulphuric acid H_2SO_5 is formed. Marshall (1890) found that on electrolysis of concentrated potassium hydrogen sulphate solution crystals of the composition KSO_4 separate at the anode.

Bredig (1893) from Ostwald's conductivity rule (p. 300) showed that the formula is $\text{K}_2\text{S}_2\text{O}_8$ and hence persulphuric acid is dibasic, and Moeller (1893) calculated van't Hoff's factor i (p. 253) from the freezing points of potassium

persulphate solutions and showed that the degree of dissociation $\alpha = (i - 1)/(n - 1)$ agrees with the conductivity value $\alpha = \lambda/\lambda_{\infty}$ when $n = 3$ ($K_2S_2O_8 = 2K^+ + S_2O_8^{2-}$).

In Marshall's experiment the HSO_4' ions discharged at the anode form persulphuric acid: $2HSO_4 = H_2S_2O_8$, and sparingly soluble potassium persulphate crystallises: $H_2S_2O_8 + 2KHSO_4 = K_2S_2O_8 + 2H_2SO_4$. Another explanation is that the HSO_4' ions are oxidised by nascent oxygen at the anode: $2HSO_4' + H_2O + O = H_2S_2O_8 + 2OH'$.

Persulphuric acid is formed by the electrolysis of 50 per cent sulphuric acid with an anode of platinum wire surrounded by a glass tube to serve as a diaphragm. The cathode is a spiral of copper wire outside the diaphragm (Fig. 269). The apparatus is immersed in ice. The addition of a little hydrochloric acid promotes the reaction. If saturated potassium hydrogen sulphate solution is used crystals of potassium persulphate separate. The solution in each experiment gives a brown colour with potassium iodide: $S_2O_8^{2-} + 2I^- = 2SO_4^{2-} + I_2$.

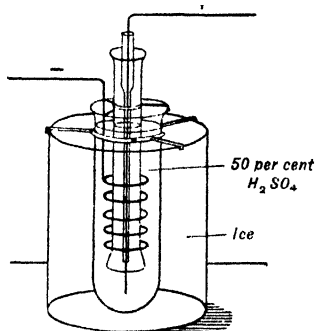
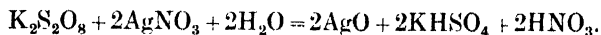


FIG. 269.—Preparation of persulphuric acid.

Ammonium persulphate $(NH_4)_2S_2O_8$ is much more soluble than the potassium salt and is made commercially by electrolysis of a solution of ammonium sulphate in sulphuric acid.

Potassium persulphate decomposes on heating: $2K_2S_2O_8 = 2K_2SO_4 + 2SO_3 + O_2$, and the solution evolves ozonised oxygen slowly in the cold and rapidly on heating: $2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2$.

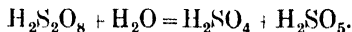
Persulphates are powerful oxidising agents, liberating iodine from potassium iodide, oxidising ferrous to ferric salts: $2Fe^{2+} + S_2O_8^{2-} = 2Fe^{3+} + 2SO_4^{2-}$, and converting chromic salts to dichromates and manganous salts to permanganates by boiling in presence of silver nitrate as a catalyst. In presence of alkali, manganous, cobalt, nickel and lead salts form higher oxides: $Mn(OH)_2 + K_2S_2O_8 = MnO_2 + 2KHSO_4$. Potassium (but not ammonium) persulphate precipitates black argentic oxide $Ag^{II}O$ from silver nitrate solution:



Many metals dissolve in persulphate solutions: $Zn + K_2S_2O_8 = ZnSO_4 + K_2SO_4$.

Ammonium persulphate is used for bleaching and for "reducing" the intensity of photographic negatives. Barium persulphate BaS_2O_8 is very soluble (separation from sulphuric acid); on boiling the solution deposits barium sulphate.

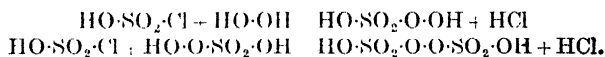
A solution of permonosulphuric acid, H_2SO_5 , which is a powerful oxidising agent, was obtained by Caro (1898) by grinding potassium persulphate with concentrated sulphuric acid, allowing to stand for an hour, and pouring on ice :



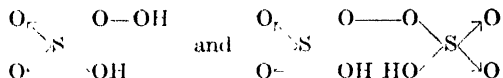
It oxidises aniline to nitrosobenzene and nitrobenzene. Baeyer and Villiger (1901) separated free sulphuric acid from the solution by shaking with barium phosphate : $Ba_3(PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 2H_3PO_4$, and differentiated Marshall's acid ($H_2S_2O_8$), Caro's acid (H_2SO_5), and hydrogen peroxide by the reactions :

1. Caro's acid instantly liberates iodine from iodides.
2. Marshall's acid only slowly liberates iodine from iodides.
3. Hydrogen peroxide at once reduces potassium permanganate, which is not changed by persulphuric acids.

In the solution of Caro's acid the ratio $SO_3 \cdot$ peroxide O was found to be 1 : 1 hence the formula is $SO_3 + O \cdot H_2O$ or H_2SO_5 , permonosulphuric acid. This was prepared nearly pure by Ahle (1909) by the action of sulphur trioxide on very concentrated hydrogen peroxide : $SO_3 + H_2O_2 = H_2SO_5$. The reaction with concentrated sulphuric acid is reversible : $H_2SO_4 + H_2O_2 \rightleftharpoons H_2SO_5 + H_2O$. D'Ans and Friedrich (1910) prepared pure permonosulphuric acid and perdisulphuric acid $H_2S_2O_8$ by the action of anhydrous hydrogen peroxide on chlorosulphonic acid :



These reactions give the conventional structural formulae :



The $S_2O_8^{2-}$ ion consists of two tetrahedral SO_4 groups joined by an oblique covalent bond (Zachariasen and Mooney, 1934).

Permonosulphuric acid is crystalline, melts at 45° , and is stable for some days. Perdisulphuric acid forms crystals stable up to 60° , but in solution slowly passes into permonosulphuric acid and sulphuric acid : $H_2O + H_2S_2O_8 = H_2SO_4 + H_2SO_5$.

No solid salts of H_2SO_5 are known, but a solution of $KHSO_5$ is said to be formed by the action of H_2O_2 on $KClSO_3$ (p. 484) : the acid should be monobasic.

Thiosulphuric acid.—Free thiosulphuric acid $H_2S_2O_3$ is not known, except possibly in solution, as it rapidly decomposes with separation of sulphur : $H_2S_2O_3 = H_2SO_3 + S$, but by boiling sulphur with an alkali sulphite solution this reaction is reversed and a solution of thiosulphate formed : $Na_2SO_3 + S = Na_2S_2O_3$. The sodium salt, discovered by Chaussier in 1799, forms large monoclinic crystals $Na_2S_2O_3 \cdot 5H_2O$,

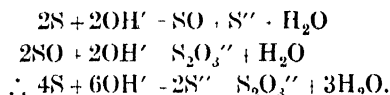
commonly called "sodium hyposulphite" or "hypo" and used in photography and as an antichlor. The stability in solution is increased by using boiled sterilised water, and adding acid sulphite ($\text{Na}_2\text{S}_2\text{O}_5$), or in volumetric solutions 0.2 gm. of Na_2CO_3 per lit.

Pure sodium thiosulphate, and especially potassium thiosulphate $\text{K}_2\text{S}_2\text{O}_3 \cdot \frac{5}{3}\text{H}_2\text{O}$, are best prepared by the interaction of alkali hydrogen sulphides and hydrogen sulphites in solution, and crystallising: $2\text{KHS} + 4\text{KHSO}_3 - 3\text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$.

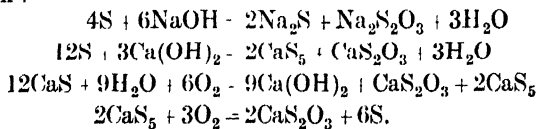
Thiosulphuric acid may be regarded (Odling, 1855) as sulphuric acid in which a hydroxyl group OH is replaced by a sulphhydryl group SH, viz. $\text{HS}\cdot\text{SO}_2\cdot\text{OH}$ (the acid $\text{HS}\cdot\text{SO}_2\cdot\text{SH}$ is unknown). Spring showed that sodium thiosulphate solution is reduced by sodium amalgam to sulphite and sulphide: $\text{NaO}\cdot\text{SO}_2\cdot\text{SNa} + 2\text{Na} - \text{NaO}\cdot\text{SO}_2\cdot\text{Na} + \text{Na}_2\text{S}$, and Bunte (1874) that ethyl sodium thiosulphate (formed by the action of ethyl bromide on a concentrated solution of sodium thiosulphate: $\text{Na}_2\text{S}_2\text{O}_3 + \text{C}_2\text{H}_5\text{Br} = \text{C}_2\text{H}_5\text{NaS}_2\text{O}_3 + \text{NaBr}$), on warming with concentrated hydrochloric acid, forms mercaptan $\text{C}_2\text{H}_5\text{SH}$, in which the ethyl group is known to be attached to sulphur:



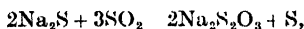
Thiosulphates and sulphides are formed by the action of alkalis on sulphur, and the reaction may be *formally* represented as a hydrolysis in which an intermediate oxide SO is formed (cf. p. 274):



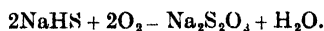
With excess of sulphur, yellow solutions containing *polysulphides* are formed: $\text{S}'' + n\text{S} - \text{S}_{n+1}''$ these also result from the oxidation of sulphide solutions by atmospheric oxygen, sulphur being also precipitated in the case of ammonium and alkaline earth sulphides: $2\text{S}'' + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{S} + 4\text{OH}'$, and $\text{S}'' + n\text{S} - \text{S}_{n+1}''$; with excess of oxygen thio-sulphate and sulphate are formed. The actual reactions are hence rather complex:



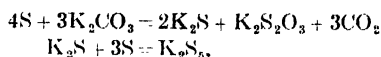
Thiosulphate is formed on passing sulphur dioxide into sulphide solutions:



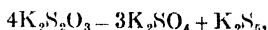
or sulphur dioxide or oxygen over heated sulphides or hydrosulphides:



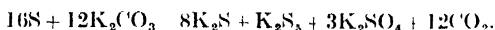
On fusing sulphur with alkalis or alkali carbonates, a dark brown mass (*liver of sulphur*) is formed. The first reactions are probably :



but much of the thiosulphate is decomposed at a higher temperature :

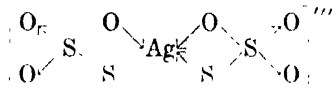


so that the final reaction is approximately



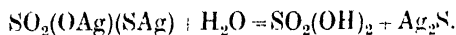
Sodium thiosulphate crystals melt at 48° and lose water at 215° ; above 223° $Na_2S_2O_3$ decomposes into sulphate and pentasulphide : $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$. At higher temperatures the Na_2S_5 loses some sulphur : $Na_2S_5 = Na_2S_4 + S$ (K_2S_5 is stable).

Most thiosulphates, except those of alkali metals, are sparingly soluble but dissolve in alkali thiosulphate solutions to form complex anions. Sodium thiosulphate solution also dissolves silver halides ($AgCl, AgBr, AgI$) forming a complex ion $Ag(S_2O_3)_2^{2-}$ or



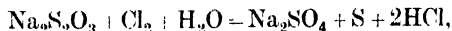
which has a sweet taste. Thiosulphate solution is used as a "fixing" agent in photography, as it dissolves unaltered silver halides (p. 743). The free acid $H[Ag(S_2O_3)]_2 \cdot H_2O$ is precipitated by concentrated nitric acid from a solution of $Na[Ag(S_2O_3)]$ in ammonia (Baines, 1929).

White precipitates of thiosulphates of silver, lead and mercury soon blacken from formation of sulphides :

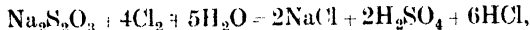


The yellow cuprous salt $Na_4[Cu_6(S_2O_3)_5] \cdot 6H_2O$, which crystallises from solutions of a cupric salt and sodium thiosulphate, decomposes on boiling to copper sulphides and sulphur. Cupric thiosulphate, however, exists as a coordination compound with ethylenediamine $[Cu(en)_2]S_2O_3$.

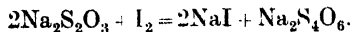
Thiosulphates are oxidised by chlorine and bromine water, and sulphur is precipitated (sodium thiosulphate is used as an *antichlor* to remove excess of chlorine from bleached fabrics) :



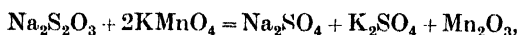
but with a large excess of halogen the sulphur is slowly oxidised to sulphuric acid :



some trithionate and tetrathionate being also formed. Iodine reacts differently, giving a *quantitative* yield of tetrathionate :



Potassium permanganate in *neutral* solution forms sulphate :



but in *acid* solution some dithionate $\text{Na}_2\text{S}_2\text{O}_6$ is also formed.

Hyposulphurous acid.—This acid $\text{H}_2\text{S}_2\text{O}_4$ must not be confused with thiosulphuric acid (formerly called hyposulphurous acid) ; it is sometimes called *hydrosulphurous acid* and the name *dithionous acid* has been proposed.

On passing sulphur dioxide into a suspension of zinc dust in absolute alcohol the metal dissolves and a solution of zinc hyposulphite is formed : $\text{Zn} + 2\text{SO}_2 = \text{ZnS}_2\text{O}_4$. The filtered solution at once bleaches indigo solution and is a powerful reducing agent. The sodium salt is formed by the action of sulphur dioxide diluted with hydrogen (the pure gas causes explosion) on sodium hydride (Moissan, 1902) : $2\text{NaH} + 2\text{SO}_2 = \text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2$, but is usually prepared by reducing an acid sulphite with zinc : $2\text{NaHSO}_3 + \text{SO}_2 + \text{Zn} = \text{Na}_2\text{S}_2\text{O}_4 + \text{ZnSO}_3 + \text{H}_2\text{O}$.

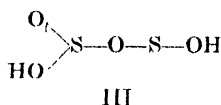
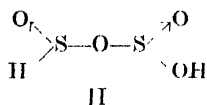
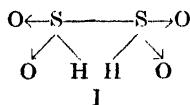
Zinc dust is added to a cooled concentrated solution of NaHSO_4 in a corked flask and sulphur dioxide passed in. Milk of lime is added to precipitate the zinc sulphite : $\text{ZnSO}_3 + \text{Ca(OH)}_2 = \text{Zn(OH)}_2 + \text{CaSO}_3$, and the filtrate is saturated with sodium chloride. The thin glassy prisms of $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ which separate oxidise rapidly to sulphite in air ; they are washed with aqueous and then anhydrous acetone and dried in a desiccator over concentrated sulphuric acid, when a white powder of $\text{Na}_2\text{S}_2\text{O}_4$ remains.

The product contains 90 per cent of $\text{Na}_2\text{S}_2\text{O}_4$ and some NaCl . It is fairly stable in air. In solution the hyposulphite decomposes to disulphite and thiosulphate : $2\text{Na}_2\text{S}_2\text{O}_4 = \text{Na}_2\text{S}_2\text{O}_5 + \text{Na}_2\text{S}_2\text{O}_4$.

Sodium hyposulphite was prepared in 1869 by Schützenberger, who formulated it as NaHSO_2 . The correct formula was established by Bernthsen (1881), who showed that for every two atoms of sulphur, *one* of oxygen is required to form a sulphite (by ammoniacal copper sulphate), and *three* atoms to form a sulphate (by a solution of iodine). These results agree with the formula S_2O_3 for the anhydride ($\text{H}_2\text{O}, \text{S}_2\text{O}_3$), but not with SO ($\text{H}_2\text{SO}_2 = \text{H}_2\text{O}, \text{SO}$) :



The structural formula I is usually adopted, although II and III have also been proposed :



Formula I accounts for the great reducing power, two hydrogen atoms linked to sulphur being present, and for the formation of some dithionate

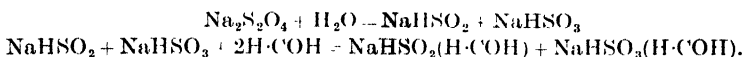
on oxidation. The doubled formula $H_2S_2O_4$ (not HSO_2) is proved by the diamagnetism of the ion S_2O_4'' (Klemm, 1937).

The free acid is supposed to be present in the yellow solution of $Na_2S_2O_4$ and oxalic acid but it rapidly decomposes into sulphurous acid and sulphur, and the colour may be due to SO (p. 488) : $2SO \rightleftharpoons SO_2 + S$.

Sodium hyposulphite is a very powerful reducing agent and is used to dissolve indigo (or other vat dyes) by forming reduced solutions :

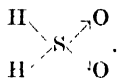


Instead of sodium hyposulphite the stable reaction product with formaldehyde, called *rongalite C*, is often used in reducing dyes. This contains a formaldehyde compound of *sodium sulphyxylate* $NaHSO_2$:



It can be made in this way or by reducing $NaHSO_3$ solution with zinc in presence of formaldehyde. The salt $NaHSO_2(H \cdot COH) \cdot 2H_2O$ can be separated by crystallisation.

Sulphoxylic acid.—Sulphoxylic acid is usually formulated as



Sulphoxylic acid H_2SO_2 is unknown but thallium sulphyxylate Tl_2SO_2 is formed by oxidising thallos sulphide with moist oxygen : $Tl_2S + O_2 \rightleftharpoons Tl_2SO_2$, and cobalt sulphyxylate is formed as a brown precipitate by the action of sodium hyposulphite and ammonia on cobalt chloride solution : $Na_2S_2O_4 + CoCl_2 \rightleftharpoons CoSO_2 + SO_2 + 2NaCl$.

Thionic acids.—The thionic acids form a group with the general formula $H_2S_nO_6$, where n is 2, 3, 4, 5, and 6. They are known only in solution but form crystalline salts. Some authors separate dithionic acid $H_2S_2O_6$ from the "true" thionic acids.

The methods of preparation are readily comprehended if it is assumed that : (i) sulphur dioxide, or acid sulphite, solutions contain the ion S_2O_5'' , (ii) acid thiosulphate solutions contain the radical $SO : S_2O_3'' + 2H^+ = 2SO + H_2O$.

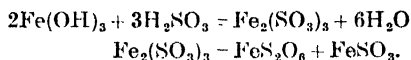
A *dithionate* is formed by oxidation of sulphur dioxide or acid sulphite solution : $S_2O_5'' + O \rightleftharpoons S_2O_6''$; a *trithionate* by the action of sulphurous acid on a thiosulphate : $S_2O_3'' + 2H^+ \rightleftharpoons 2SO + H_2O$ and $SO + S_2O_5'' = S_3O_6''$; a *tetrathionate* by oxidation of a thiosulphate : $2S_2O_3'' = S_4O_6'' + 2e$; and a solution of *pentathionic acid* by the action of hydrogen sulphide on sulphurous acid : $H_2S + 2SO_2 \rightleftharpoons 3SO + H_2O$ and $5SO + H_2O \rightleftharpoons H_2S_5O_6$.

Dithionic acid $H_2S_2O_6$, discovered by Gay-Lussac and Welter in 1819, is formed by the action of mild oxidising agents, such as a suspension of manganese dioxide, on sulphurous acid : $S_2O_5'' + O = S_2O_6''$.

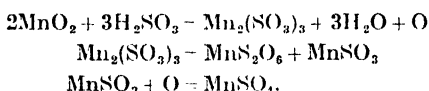
Sulphur dioxide is slowly passed into a suspension of *finely ground crystalline native manganese dioxide (pyrolusite)* in water, cooled in ice.

Manganous dithionate and manganous sulphate are formed: $\text{MnO}_2 + 2\text{SO}_2 = \text{MnS}_2\text{O}_6$; $\text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4$. When all the pyrolusite has reacted, hot saturated baryta water is added to precipitate all the manganese as $\text{Mn}(\text{OH})_2$ and the sulphate as BaSO_4 , which are filtered and washed with hot water. The slight excess of baryta in the filtrate is precipitated by carbon dioxide, and the filtrate is evaporated to give colourless monoclinic crystals of barium dithionate, $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$.

With a suspension of ferric hydroxide a brownish-red solution of ferric sulphite is formed, which passes into a pale green solution of ferrous dithionate and sulphite:



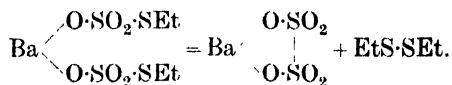
Cobaltic hydroxide reacts similarly, and the reaction with manganose dioxide may be:



Dithionic acid is obtained by an oxidation reaction and (unlike the other thionic acids) it is oxidised only with difficulty; boiling concentrated hydrochloric acid and potassium bromate slowly oxidise it to sulphate. Dithionates, unlike salts of higher thionic acids, are not decomposed by sulphides and sulphites. They are all soluble and mostly crystallise with water: no acid salts are known. They may be made by decomposing barium dithionate solution with the metal sulphate or carbonate, filtering from barium sulphate or carbonate, and crystallising: $\text{Na}_2\text{S}_2\text{O}_6$, $\text{K}_2\text{S}_2\text{O}_6$, $\text{CaS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$, $\text{ZnS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, $\text{Al}_2(\text{S}_2\text{O}_6)_3 \cdot 18\text{H}_2\text{O}$, $\text{PbS}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$, $\text{Cr}_2(\text{S}_2\text{O}_6)_3 \cdot 18\text{H}_2\text{O}$. A solution of dithionic acid is prepared by precipitating barium dithionate solution with dilute sulphuric acid and concentrating on a water bath and then in vacuum over sulphuric acid; above a sp. gr. of 1.347 it decomposes: $\text{H}_2\text{S}_2\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2$. The salts decompose similarly on heating: $\text{K}_2\text{S}_2\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2$.

By the action of sodium amalgam on dithionate solution a sulphite is formed: $\text{S}_2\text{O}_6'' + 2\text{Na} = 2\text{SO}_3'' + 2\text{Na}$.

Barium ethyl thiosulphate, formed on adding barium chloride to sodium ethyl thiosulphate solution, rapidly forms barium dithionate and ethyl sulphide (Ramsay, 1875):



Trithionic acid $\text{H}_2\text{S}_3\text{O}_6$ was discovered by Langlois (1842), who obtained potassium trithionate by warming a saturated solution of potassium hydrogen sulphite with powdered sulphur for three or four days:

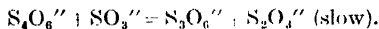
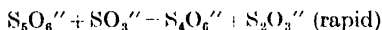


The best method of preparation (Plessy, 1844 ; Hertlein, 1896) is to pass sulphur dioxide into a saturated solution of potassium thiosulphate until a yellow colour develops, allow to stand till colourless, and repeat until no colour forms. On standing the salt crystallises. The reaction, usually formulated : $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$, is more complex; less sulphur separates and some tetra- and pentathionate are formed. A trithionate is formed by oxidising ice-cold saturated sodium thiosulphate solution with hydrogen peroxide :

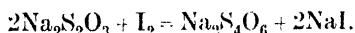


A solution of *trithionic acid*, prepared by precipitating a concentrated solution of $K_2S_3O_6$ with tartaric, perchloric or hydrofluosilicic acid, decomposes easily on concentration : $H_2S_3O_6 = H_2SO_4 + SO_2 + S$, and the salts also decompose on heating : $K_2S_3O_6 = K_2SO_4 + SO_2 + S$. Trithionates, except the silver, mercurous and mercuric salts, are soluble.

Sodium amalgam reacts with a trithionate solution to form sulphite and thiosulphate : $S_3O_6'' + 2Na = SO_3'' + S_2O_3'' + 2Na'$, and alkali sulphide forms thiosulphate : $S_3O_6'' + S'' = 2S_2O_3''$. A sulphite does *not* react with a trithionate, but removes sulphur from a pentathionate and from a tetrathionate, forming a tetrathionate and trithionate, respectively, and a thiosulphate :

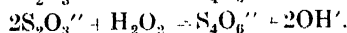
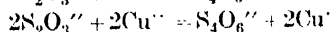


Tetrathionic acid $H_2S_4O_6$ was discovered by Fordos and Gélis in 1843. The sodium salt is formed in the iodine-thiosulphate titration :

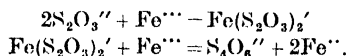


To obtain the pure salt a saturated solution of sodium thiosulphate is added drop by drop to a cooled solution of iodine in alcohol, shaking after each addition, until only a pale yellow colour remains. The tetrathionate separates in crystals (sometimes first as an oily concentrated solution) and is washed with alcohol, dissolved in water, reprecipitated with alcohol and dried over sulphuric acid. In solution it slowly decomposes : $Na_2S_4O_6 = Na_2SO_4 + SO_2 + 2S$, and the reaction is accelerated by sodium thiosulphate.

The tetrathionate is formed by *oxidation* of two thiosulphate ions, two electrons being removed : $2S_2O_3'' = S_4O_6'' + 2e$. The reaction is quantitative with iodine, but with other mild oxidising agents some sulphate is also formed :



On adding ferric chloride to sodium thiosulphate solution, a deep purple colour due to the ion $\text{Fe}(\text{S}_2\text{O}_3)_2'$ rapidly disappears and a colourless solution free from ferric ions (no colour with KCNS) is formed :

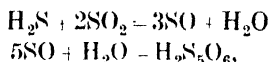


Tetrathionate produced in electrolytic oxidation of thiosulphate solution is probably formed by the action of hydrogen peroxide at the anode.

With tetrathionate solution sodium amalgam forms thiosulphate : $\text{S}_4\text{O}_6'' + 2\text{Na} = 2\text{S}_2\text{O}_3'' + 2\text{Na}'$ (reverse of formation of $\text{S}_4\text{O}_6''$ from $2\text{S}_2\text{O}_3''$), sulphides form thiosulphate and sulphur : $\text{S}_4\text{O}_6'' + \text{S}'' = 2\text{S}_2\text{O}_3'' + \text{S}$, and sulphites slowly form trithionate : $\text{S}_4\text{O}_6'' + \text{SO}_3'' = \text{S}_3\text{O}_6'' + \text{S}_2\text{O}_3''$. The tetrathionates are soluble.

Lead acetate and sodium thiosulphate solution precipitate white lead thiosulphate. A suspension of this reacts with iodine to form a solution of lead tetrathionate : $2\text{PbS}_2\text{O}_3 + \text{I}_2 = \text{PbI}_2 + \text{PbS}_4\text{O}_6$, which when filtered and precipitated with dilute sulphuric acid gives a solution of tetrathionic acid. This is fairly stable and can be concentrated on a water bath and in vacuum over sulphuric acid up to a point, but then decomposes : $\text{H}_2\text{S}_4\text{O}_6 = \text{H}_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$. The tetrathionates decompose on heating : $\text{K}_2\text{S}_4\text{O}_6 = \text{K}_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$.

Pentathionic acid $\text{H}_2\text{S}_5\text{O}_6$, discovered by Wackenroder in 1845, is formed by the interaction of hydrogen sulphide and sulphurous acid in solution, sulphur and tetrathionic acid being also formed. It is possible that the oxide SO is an intermediate product :



the $\text{S}_5\text{O}_6''$ ions being partly reduced to $\text{S}_4\text{O}_6''$ by SO_3'' ions.

Pentathionic acid (the existence of which was doubted) was studied by Debus (1888) in a masterly research on the thionic acids. The salts are not stable unless a little hydrochloric or sulphuric acid is added to the solution.

Hydrogen sulphide is passed slowly for a few hours a day into saturated sulphur dioxide solution till all the SO_2 finally disappears. The milky liquid (*Wackenroder's solution*) contains suspended and colloidal sulphur, and pentathionic and tetrathionic acids. These are decomposed by alkali, so that only one-third of the amount of KOH required for neutralisation is run into the liquid in a thin stream with constant stirring. Potassium acetate or bicarbonate may be used instead. On spontaneous evaporation $\text{K}_2\text{S}_4\text{O}_6$ (monoclinic) and $\text{K}_2\text{S}_5\text{O}_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ (rhombic) crystals form, and may be separated by hand-picking, or (when well-formed) by flotation in a mixture of bromoform and xylene of density 2.2, when $\text{K}_2\text{S}_4\text{O}_6$ sinks and $\text{K}_2\text{S}_5\text{O}_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ floats. The pentathionate may be recrystallised from warm water acidified with sulphuric acid.

Pentathionate is formed by the action of concentrated hydrochloric acid on concentrated sodium thiosulphate solution containing a little sodium arsenite and cooled at -10° (Raschig): $S_2O_3'' + 2H^{\cdot} = 2SO + H_2O$; $5SO + H_2O = H_2S_5O_6$. The filtered liquid deposits crystals of $Na_2S_5O_6$ and the filtrate contains $H_2S_5O_6$, giving crystals of $K_2S_5O_6$, $1\frac{1}{2}H_2O$ on adding potassium acetate.

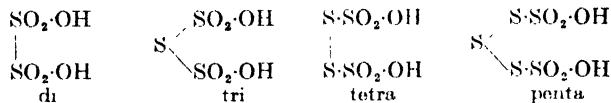
A solution of pentathionic acid is prepared by precipitating a solution of the potassium salt with tartaric acid; it may be concentrated on a water bath to density 1.3 and in a vacuum desiccator to density 1.6, but then decomposes: $H_2S_5O_6 = H_2SO_4 + SO_2 + 3S$. The salts, which are soluble, decompose on heating: $K_2S_5O_6 = K_2SO_4 + SO_2 + 3S$.

Potassium amalgam reduces pentathionate to tetrathionate and finally to thiosulphate: $S_5O_6'' - 2K = S_4O_6'' + 2K^{\cdot} + S''$, and $S_4O_6'' + 2K = 2S_2O_3'' + 2K^{\cdot}$; sulphide forms thiosulphate and sulphur: $S_5O_6'' + S'' = 2S_2O_3'' + 2S$; and sulphite forms tetrathionate and thiosulphate: $S_5O_6'' + SO_3'' = S_4O_6'' + S_2O_3''$.

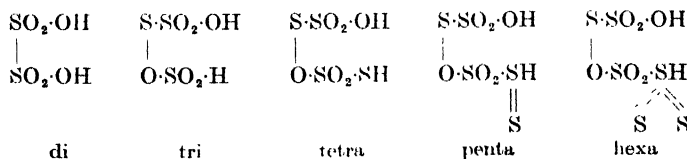
Hexathionic acid $H_2S_6O_6$, according to Debus, is contained in Wackenroder's solution, from which, after separation of $K_2S_4O_6$ and $K_2S_5O_6$, he obtained warty crusts of $K_2S_6O_6$. The potassium salt is prepared (Weitz and Aelterberg, 1928) by adding a solution of 1 mol of potassium nitrite and 3 mols of potassium thiosulphate to well-cooled hydrochloric acid in a large flask, with vigorous shaking, the oxides of nitrogen being removed by a current of air, and the solution cooled in a freezing mixture. Potassium chloride separates and is removed. On concentrating the solution under reduced pressure, potassium hexathionate crystallises.

Hexathionic acid is formed by the action of a large quantity of concentrated hydrochloric acid on a solution of sodium thiosulphate containing sodium arsenite, and may be isolated as potassium hexathionate by adding potassium acetate after concentration (Kurtenacker and Matejka, 1936).

Structures of the thionic acids. Several sets of formulae have been proposed for the thionic acids. Blomstrand (1869) and Mendeléeff (1870) suggested that $-SO_2OH$ groups are linked by sulphur atoms:



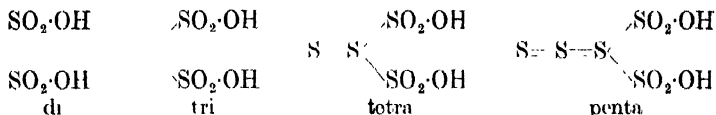
Debus (1888) considered that the central linking group was $-S-O-$:



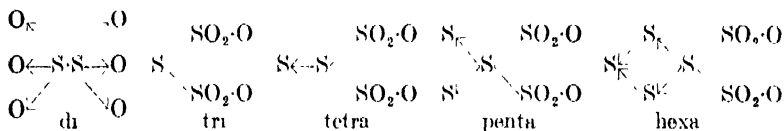
Hertlein (1896) found that polythionates of mercury and silver do not form complex compounds, and from this and the molecular refractions of the salts he concluded that the metal is attached to oxygen as in Blom-

strand's and Mendeléoff's formulae, rather than to sulphur as in Debus's formulae, since these metals in combination with sulphur readily form complex compounds.

Vogel (1925) proposed the formulae :



which are similar to those now adopted, those for di- and tri-thionates being based on X-ray evidence ; the ions are :

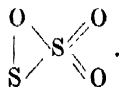


The dithionate ion is a trigonal bipyramid, and the ---S angle in the trithionate ion is about 103° .

Although dithionic acid does not form acid salts, the conductivities of the sodium salt and Ostwald's rule (p. 300), and also the diamagnetism of the sodium salt, show that the acid is dibasic, $\text{H}_2\text{S}_2\text{O}_6$ and not HSO_3 .

Sulphur monoxide. -- This oxide, SO , is formed by (i) the slow oxidation of sulphur on heating in air, (ii) burning sulphur in oxygen below 40 mm. pressure, (iii) the action of an electric discharge on a mixture of sulphur dioxide and sulphur vapour at 10 mm. pressure : $\text{SO}_2 + \text{S} \rightarrow 2\text{SO}$, (iv) the action of finely-divided silver on thionyl chloride : $\text{SOCl}_2 + 2\text{Ag} \rightarrow \text{SO} + 2\text{AgCl}$ (Cordes and Schenk, 1933). It is a colourless gas, stable at room temperature but decomposing at 100° : $2\text{SO} \rightarrow \text{SO}_2 + \text{S}$. It combines with oxygen on sparking, and readily with chlorine at low pressure : $\text{SO} + \text{Cl}_2 \rightarrow \text{SOCl}_2$. Alkali absorbs it to form sulphide, sulphite and thiosulphate. An orange-red solid formed on cooling the gas with liquid air does not form SO on warming.

Sulphur sesquioxide. Powdered sulphur dissolves in fuming sulphuric acid to form an indigo-blue liquid. The malachite-green solid sulphur sesquioxide is formed by the action of liquid sulphur trioxide on powdered sulphur : $\text{SO}_3 + \text{S} = \text{S}_2\text{O}_3$ (Weber, 1875 ; Partington and Vogel, 1925). It is unstable, decomposing at room temperature and rapidly on warming : $2\text{S}_2\text{O}_3 \rightarrow \text{S} + 3\text{SO}_2$, and is decomposed by water, forming sulphur, sulphuric acid and trithionic acid, with smaller amounts of sulphurous and pentathionic acids. The formula may be



CHAPTER XXVIII

SELENIUM AND TELLURIUM

Selenium.—Selenium was discovered by Berzelius in 1817 in a deposit in a lead chamber making sulphuric acid. The name is from the Greek *selene*, the moon, on account of the analogy of the element with tellurium, named from the Latin *tellus*, the earth. Many important compounds of selenium were discovered by Berzelius; selenic acid was discovered by Mitscherlich in 1827. Selenium is intermediate between sulphur and tellurium in its properties.

Selenium occurs native in Mexico and California, and in some native sulphur, particularly Japanese; selenides of lead $PbSe$, copper Cu_2Se and silver Ag_2Se occur at Clausthal (Harz), mercury selenide Hg_2Se in Mexico, and the important ore *zorgite*, a double selenide of copper and lead with some iron and silver and as much as 31 per cent of Se, in the Argentine. *Crookesite* $(Cu, Tl, Ag)_2Se$ is found at Skrikerum in Sweden. Many kinds of pyrites contain selenium, which finds its way into the flue dusts and chamber deposits of sulphuric acid works and into the commercial acid. In making sodium sulphate with this acid (p. 210) the selenium passes as chloride into the hydrochloric acid. Selenium occurs in soil of the arid plains of Dakota, Wyoming and Kansas, making the herbage poisonous to animals, and it may pass into wheat. Most vegetables (especially spinach), and bones and teeth, contain it in traces.

Selenium may be extracted from vitriol chamber deposits, etc., by digesting with fuming sulphuric acid: $Se + 2SO_3 = SeO_2 + 2SO_2$, or with potassium cyanide solution when it dissolves as potassium selenocyanate: $KCN + Se = KCNSe$, and on adding hydrochloric acid selenium is precipitated as a red powder: $KCNSe + HCl = KCl + HCN + Se$. It is purified by distillation or by evaporation to dryness with nitric acid, when solid selenium dioxide SeO_2 is formed, which can be sublimed, or recrystallised as selenious acid H_2SeO_3 , a solution of which is reduced by sulphur dioxide: $H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4$.

Selenium is extracted from the anode slimes of electrolytic copper refining (p. 721) which may contain as much as 96 per cent together with tellurium, although 1 to 18 per cent Se and 0.25 to 2.5 per cent Te are usual.

Selenium is used in making red glass, enamels and glazes, and the pigment cadmium selenide CdSe , and in photoelectric cells; its red compounds are used in photographic toning and selenobenzamide in froth flotation. Selenium has been used in vulcanising rubber; in conjunction with sulphur it prevents surface crystallisation or "bloom."

Like sulphur, selenium exists in several *allotropic modifications* (Saunders, 1900):

1. **Amorphous selenium.** (a) *Vitreous selenium*, an opaque almost black lustrous solid, sp. gr. 4.28, giving a red powder, and formed by suddenly cooling melted selenium. It softens at 50° and if rapidly heated to 220° is liquid but viscous. Above 60° – 80° it changes fairly quickly into *metallic selenium* (no. 3). (b) *Red amorphous selenium*, a dark red powder, sp. gr. 4.26, precipitated from a solution of selenious acid by sulphur dioxide, or by hydrochloric acid from a solution of KCNSe , or formed (as "flowers of selenium") by subliming selenium in a sealed tube. Amorphous selenium is slightly soluble in carbon disulphide (about 0.1 per cent at the b.pt.) and readily in selenium oxychloride. (c) *Colloidal selenium*, formed as a red sol by mixing dilute solutions of selenious and sulphurous acids.

2. **Monoclinic selenium** is obtained in red crystals by letting forms 1a or 1b stand in contact with carbon disulphide. Two stable crystalline varieties are known, sp. gr. 4.47 (cf. β -sulphur). If heated rapidly the red crystals fuse at 200° with partial conversion into metallic selenium, and the meta-stable melting point is probably 170 – 180° (cf. α -sulphur).

3. **Metallic selenium** is formed, with evolution of heat, when any other variety is heated at 200 – 220° for some time. It is silvery-grey, sp. gr. 4.80, gives a black powder (red if very fine), and is insoluble in carbon disulphide (about 1 per cent of soluble selenium is always present) but soluble in chloroform. It has been obtained by sublimation in hexagonal crystals isomorphous with tellurium.

The electrical conductivity of metallic selenium is very small in the dark, but on exposure to light it increases rapidly, the original conductivity being recovered (with a time-lag) in the dark (Willoughby Smith, 1873). This property, which is probably due to an inner photoelectric effect (liberation of electrons in the surface layer of the solid) is utilised in photoelectric cells.

Briegleb (1929) from X-ray examination concluded that vitreous selenium is amorphous, monoclinic selenium consists mostly of Se_2 molecules, and metallic selenium mostly of Se molecules.

Selenium boils at 684.8° giving a dark-red vapour, the density of which falls with rise of temperature; at lower temperatures Se_8 and Se_6 molecules seem to be present, above 1400° Se_2 molecules only. The molecular weight in solution in phosphorus corresponds with Se_8 .

Selenium combines with many metals to form *selenides*, and alkali metal selenides and polyselenides, Na_2Se , Na_2Se_2 , Na_2Se_3 , Na_2Se_4 and Na_2Se_5 , analogous to the sulphides are formed. It reduces hot silver nitrate solution: $3\text{Se} + 4\text{AgNO}_3 + 3\text{H}_2\text{O} = 2\text{Ag}_2\text{Se} + \text{H}_2\text{SeO}_3 + 4\text{HNO}_3$.

Hydrogen selenide H_2Se is formed in small amounts on heating selenium in hydrogen: $\text{H}_2 + \text{Se} \rightleftharpoons \text{H}_2\text{Se}$ (although most of the selenium

sublimes in glittering crystals) and by the action of nascent hydrogen on selenious acid. On heating iron filings with selenium, ferrous selenide is formed, which gives H_2Se with acids: $\text{FeSe} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{Se}$. Pure H_2Se is obtained by the action of water on aluminium selenide: $\text{Al}_2\text{Se}_3 + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{Se}$. Hydrogen selenide is a colourless inflammable gas with a very offensive smell and strong action on the mucous membranes and is poisonous. It is less stable than hydrogen sulphide. It is soluble in water to a feebly acid solution which precipitates selenides of many metals, and oxidises on exposure to air, selenium being precipitated. It combines with ammonia gas to form solid $(\text{NH}_4)_2\text{Se}$. The normal density of the gas is 3.6696 gm./lit., corresponding with a molecular weight 82, and it leaves its own volume of hydrogen when decomposed by heated tin, hence the formula is H_2Se . The b.pt. is -41.7° and the m.pt. -64° .

Halogen compounds of selenium.—Selenium forms two fluorides, SeF_6 (colourless gas) and SeF_4 (colourless liquid), and a liquid oxyfluoride SeOF_2 . The reddish-brown liquid selenium monochloride Se_2Cl_2 is formed by passing chlorine over selenium. It decomposes on heating, giving the more stable tetrachloride: $2\text{Se}_2\text{Cl}_2 = 3\text{Se} + \text{SeCl}_4$, and is slowly decomposed by water: $2\text{Se}_2\text{Cl}_2 + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 3\text{Se} + 4\text{HCl}$. The pale yellow solid selenium tetrachloride SeCl_4 is formed by the action of excess of chlorine on selenium, or by heating selenium dioxide and PCl_5 , distilling off the POCl_3 in a current of carbon dioxide, and subliming: $\text{SeO}_2 + 2\text{PCl}_5 = \text{SeCl}_4 + 2\text{POCl}_3$. It sublimes without fusion and the yellow vapour is dissociated: $2\text{SeCl}_4 \rightleftharpoons \text{Se}_2\text{Cl}_2 + 3\text{Cl}_2$. It is decomposed by water: $\text{SeCl}_4 + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 4\text{HCl}$.

The light-yellow liquid selenium oxychloride SeOCl_2 is formed by the partial hydrolysis of the tetrachloride: $\text{SeCl}_4 + \text{H}_2\text{O} = \text{SeOCl}_2 + 2\text{HCl}$, and on heating the dioxide and tetrachloride in a sealed tube: $\text{SeO}_2 + \text{SeCl}_4 = 2\text{SeOCl}_2$. The liquid has a high dielectric constant (46.2), mixes with many organic liquids and reacts with most metals and oxides; potassium reacts explosively but sodium is unaffected.

The reddish-brown liquid selenium monobromide Se_2Br_2 is more stable than the orange-red solid selenium tetrabromide SeBr_4 . Both are formed from the elements. The solid acid H_2SeBr_6 and salts are known.

The very reactive selenium oxybromide SeOBr_2 is obtained by distilling SeOCl_2 with NaBr , or by mixing together Se , SeO_2 and 2Br_2 and warming. No iodides of selenium are known.

Oxides and oxyacids of selenium.—Selenium burns, but not very easily, when heated in air, and more readily in oxygen, with a blue flame forming white crystalline volatile selenium dioxide SeO_2 , very soluble in water. SeO_2 on heating forms a yellow liquid and vapour. The vapour density is normal, but in solution in SeOCl_2 the molecule is $(\text{SeO}_2)_3$.

By evaporating a solution of SeO_2 in water, or selenium in hot nitric acid, very soluble hexagonal prisms of selenious acid H_2SeO_3 are formed. It gives acid and normal selenites *e.g.* KHSeO_3 and K_2SeO_3 , and superacid salts, $\text{KH}_4(\text{SeO}_3)_2$. Heteropolyacids are formed with vanadic, molybdic and uranic acids. CaSeO_3 and BaSeO_3 are sparingly soluble. Selenious acid and selenites are easily reduced to red selenium, *e.g.* by organic matter in dust.

Selenium trioxide SeO_3 is formed, mixed with some SeO_2 , as a white deliquescent solid by passing a glow discharge through a mixture of oxygen and selenium vapour at 4 mm. pressure. The corresponding selenic acid H_2SeO_4 is produced by the action of chlorine on selenium or selenious acid suspended in water: $\text{Se} + 4\text{H}_2\text{O} + 3\text{Cl}_2 = \text{H}_2\text{SeO}_4 + 6\text{HCl}$: by the action of bromine on silver selenite in water: $\text{Ag}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Br}_2 = 2\text{AgBr} + \text{H}_2\text{SeO}_4$: by oxidising selenious acid in nitric acid with chloric acid, or selenious acid with permanganate, or by electrolytic oxidation. The solution may be evaporated until at 265° it contains 95 per cent of H_2SeO_4 , when it decomposes on further heating: $2\text{H}_2\text{SeO}_4 = 2\text{H}_2\text{SeO}_3 + \text{O}_2$. If this liquid is placed over sulphuric acid in a vacuum desiccator until it contains 97.4 per cent of H_2SeO_4 (sp. gr. 2.627) and then strongly cooled, it forms colourless hexagonal crystals of pure selenic acid, m.pt. 58° . The acid is very hygroscopic and evolves heat with water: the concentrated acid chars organic matter and dissolves sulphur to a blue liquid. Potassium selenate is formed on fusing selenium with nitre (Mitscherlich, 1827) and sodium selenate on heating selenium with sodium peroxide. (Nitric acid oxidises selenium only to *selenious acid*.)

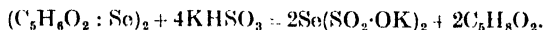
Selenic acid on heating dissolves copper and gold, forming CuSeO_4 and $\text{Au}_2(\text{SeO}_4)_3$, part of the acid being reduced to selenious acid. The dilute acid dissolves zinc: $\text{Zn} + \text{H}_2\text{SeO}_4 = \text{ZnSeO}_4 + \text{H}_2$, but iron receives a thin protective coating of selenium and is not dissolved. Calcium selenate forms a hemihydrate $\text{CaSeO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, like plaster of Paris. Barium selenate is rather more soluble in water than barium sulphate and occludes salts more easily.

According to Mitscherlich selenic acid is not reduced by hydrogen sulphide or sulphur dioxide, but Bengel (1927) says it is reduced, with some difficulty. It is reduced to selenious acid by boiling with dilute hydrochloric acid: $\text{H}_2\text{SeO}_4 + 2\text{HCl} = \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} + \text{Cl}_2$.

Selenium dissolves in fused sulphur trioxide or fuming sulphuric acid, more easily on warming, to a green solution containing selenosulphur trioxide SSeO_3 (sulphur gives a blue solution of S_2O_3 and tellurium a red solution of STeO_3).

Selenium dissolves in potassium sulphite solution forming potassium selenothiosulphate K_2SSeO_3 (analogous to the thiosulphate), which can be obtained in colourless crystals.

Salts of selenotriithionic acid $\text{Se}(\text{SO}_2\cdot\text{OH})_2$ are formed by the action of selenium acetylacetonone (from acetylacetonone and SeCl_4) on alkali hydrogen sulphites :



A solution of the free acid is formed from selenium acetylacetonone and sulphurous acid. A salt of selenopentathionic acid $\text{H}_2\text{SeS}_4\text{O}_6$ is formed from selenious acid and sodium thiosulphate in weakly acid solution : $\text{SeO}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 : 4\text{HCl} = 4\text{NaCl} + \text{Na}_2\text{S}_4\text{O}_6 + \text{Na}_2\text{SeS}_4\text{O}_6 + 2\text{H}_2\text{O}$.

An explosive orange-red selenium nitride Se_4N_4 (cf. S_4N_4) is precipitated on passing dry ammonia into a dilute solution of SeOCl_2 in benzene, or by the action of liquid ammonia on SeBr_4 in presence of CS_2 (Strecker and Claus, 1923). Selenophen $\text{C}_6\text{H}_5\text{Se}$ (analogous to thiophen) is formed from selenium and acetylene at 400° (Briscoe and Peel, 1928).

Tellurium.—Native tellurium occurs in small amounts and was called by early mineralogists *aurum paradoxum* or *aurum problematicum*, on account of its lustre. J. F. Müller von Reichenstein in 1782 sent a specimen of it to Bergman, who reported that it was a peculiar metal similar to antimony. Klaproth in 1798 examined it and called it tellurium (Latin *tellus*, the earth). Berzelius in 1832, after a thorough investigation characteristic of his work, pointed out its analogies to sulphur and selenium (which he had discovered in 1817).

Tellurium is rather rare. It is found native in Central Europe, Colorado and Bolivia, and with selenium in Japanese sulphur, but usually occurs as tellurides : *sybranite* or *graphic tellurium* $(\text{Ag}, \text{Au})\text{Te}_2$, *nagyagite* or *black tellurium* $(\text{Au}, \text{Pb})_2(\text{Te}, \text{S}, \text{Sb})_3$, *hessite* Ag_2Te , and *tetradymite* Bi_2Te_3 . Gold tellurides are important for gold extraction in Australia and Colorado.

Tellurium may be extracted from some silver and bismuth ores, or from the anode slimes of copper refining (p. 721). Less than 0.1 per cent gives lead a greater tensile strength and resistance to acids, and tellurium has also been proposed for use as a dark finish in electroplating silver, for compounding rubber, and as diethyl telluride as an anti-knock for petrol. It seems, however, to find little use, since its compounds have offensive properties.

Bismuth ores are dissolved in hydrochloric acid, tellurium precipitated with sodium sulphite, and purified by boiling with sodium sulphide solution and powdered sulphur, then adding sodium sulphite, when tellurium separates as a greyish-black precipitate, which becomes silver-white on fusion.

Tellurium can be deposited in smooth thick layers on a lead cathode from a solution of TeO_2 in hydrofluoric and sulphuric acids ; with a tellurium anode containing selenium, the latter deposits as a slime (Mathers and Turner, 1928).

A red colloidal solution obtained by reducing telluric acid with hydrazine behaves towards electrolytes like a metal sol (Doolan, 1925).

Tellurium forms hexagonal crystals, is brittle and easily powdered, has a bright lustre like antimony, a fairly high sp. gr. of 6.31, conducts electricity like a metal, and readily forms an amalgam. An amorphous variety, sp. gr. 6.015, is precipitated by sulphur dioxide from tellurous or telluric acid. Tellurium melts at 449.8°, and boils at 1390° (478° in a nearly perfect vacuum) forming a golden-yellow vapour. At 671° the vapour pressure is only 15 mm. The vapour density at 1400° is slightly higher than corresponds with Te₂. When heated in air tellurium burns with a blue flame forming white vapours of tellurium dioxide TeO₂: it burns, when heated, even in very dry oxygen.

Tellurium combines with many metals to form *tellurides*, and dark-red alkali polytellurides.

Hydrogen telluride H₂Te, prepared in an impure state by Davy in 1810 from zinc telluride and acid, is obtained pure from aluminium telluride and dilute hydrochloric acid, or by the electrolysis of 50 per cent sulphuric or phosphoric acid at -20° with a tellurium cathode, and at once drying and liquefying the gas (b.pt. -1.8°, m.pt. -57°).

Hydrogen telluride is a colourless gas with an unpleasant smell, less stable than hydrogen selenide but fairly stable in the dark when pure. Exposure to light decomposes it, especially when moist: H₂Te = H₂ + Te. An equal volume of hydrogen remains after heating with zinc, and this result, with the gas density, gives the formula H₂Te. The gas burns in air with a pale blue flame: 2H₂Te + 3O₂ = 2H₂O + 2TeO₂. The solution oxidises in air and becomes red, from separation of tellurium.

Hydrogen telluride is a fairly strong acid and hydrogen selenide is stronger than hydrogen sulphide: the acidic character increases with atomic weight in the group S, Se, Te.

Halogen compounds of tellurium.—Tellurium combines with fluorine with incandescence to form colourless gaseous tellurium hexafluoride TeF₆, and tellurium oxyfluoride, TeOF₂. $\frac{1}{2}$ H₂O, is formed in white crystals by the action of anhydrous hydrofluoric acid on TeO₂. The hexafluoride is only slowly hydrolysed by water: TeF₆ + 6H₂O = 6HF + H₆TeO₆ (telluric acid). Excess of chlorine forms with tellurium the stable white crystalline tellurium tetrachloride TeCl₄, very hygroscopic and hydrolysed by water: TeCl₄ + 2H₂O = TeO₂ + 4HCl. The vapour is stable at 530°. On heating TeCl₄ with tellurium, black solid tellurium dichloride TeCl₂ is formed. TeCl₄ and hydrochloric acid form H₂TeCl₆, salts of which (*e.g.* K₂TeCl₆) are isomorphous with corresponding stannic, plumbic and platinum compounds and with K₂SiF₆.

Tellurium forms a dibromide TeBr₂ and tetrabromide TeBr₄, and (unlike sulphur and selenium) a tetraiodide TeI₄, formed from the elements in iron-grey crystals and also in solution by the reaction TeO₂ + 4HI = TeI₄ + 2H₂O.

Oxides of oxyacids of tellurium.—Tellurium forms the oxides TeO , TeO_2 and TeO_3 ; tellurous acid is known as salts, the tellurites, e.g. K_2TeO_3 ; ordinary telluric acid is H_6TeO_6 .

Black tellurium monoxide TeO is formed by heating STeO_3 (see below) in vacuum at 230° : $\text{STeO}_3 = \text{TeO} + \text{SO}_2$. With concentrated sulphuric acid it forms white crystals of tellurium sulphate: $2\text{TeO} + 3\text{H}_2\text{SO}_4 = \text{Te}(\text{SO}_4)_2 + \text{STeO}_3 + 3\text{H}_2\text{O}$.

The white crystalline solid tellurium dioxide TeO_2 , formed by burning tellurium in air or oxygen, or by evaporation with nitric acid and heating the basic nitrate $2\text{TeO}_2, \text{HNO}_3$, is only sparingly soluble and has no acid reaction. It dissolves in alkalis forming tellurites, e.g. K_2TeO_3 , from which acids precipitate a hydrated form called tellurous acid, which reddens litmus. Tellurites are also formed by fusing TeO_2 with alkalis or alkali carbonates. The formation of the basic nitrate $2\text{TeO}_2, \text{HNO}_3$ or $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$ (rhombic crystals) by evaporating tellurium or the dioxide with nitric acid, shows that TeO_2 is amphoteric.

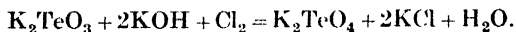
Tellurium trioxide TeO_3 is an orange-yellow powder formed on heating telluric acid. It decomposes when strongly heated: $2\text{TeO}_3 = 2\text{TeO}_2 + \text{O}_2$. It is insoluble in water, but telluric acid is formed in other ways.

Telluric acid is best prepared by dissolving tellurium powder in aqua regia, adding chloric acid in small portions, evaporating in vacuum, precipitating with nitric acid, and recrystallising from water. It forms white crystals of the composition H_6TeO_6 , in two crystalline forms, cubic and monoclinic. Telluric acid is sparingly soluble in cold but readily in hot water. It is a weak acid.

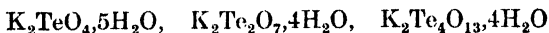
The molecular weight in solution corresponds with H_6TeO_6 , and thin plates of the crystals, unlike true hydrates (e.g. $\text{CuSO}_4, 5\text{H}_2\text{O}$) are not permeated by water vapour. The methyl ester $\text{Te}(\text{OCH}_3)_6$ and silver salt Ag_6TeO_6 are known, hence the acid is H_6TeO_6 and not $\text{H}_2\text{TeO}_4, 2\text{H}_2\text{O}$. The X-rays show that the TeO_6 radical is octahedral. Below 10° the solution of telluric acid deposits the hydrate $\text{H}_2\text{TeO}_4, 6\text{H}_2\text{O}$.

On heating H_6TeO_6 in a sealed tube at 140° it forms allotelluric acid (H_2TeO_4)₂, a fairly strong acid. At 100° – 220° H_6TeO_6 loses water and forms a white powder of metatelluric acid (H_2TeO_4)₃.

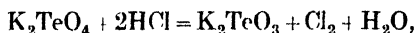
The tellurates are formed by fusing tellurites with potassium nitrate or passing chlorine into alkaline solutions of tellurites:



They are not isomorphous with sulphates or selenates. Some tellurates exist in two forms, a colourless salt soluble in water and acids and a yellow insoluble form. Normal, acid, and superacid salts are known:



(cf. chromates and polychromates). Tellurates are reduced to tellurites by boiling hydrochloric acid :



and (unlike selenates) are easily reduced to tellurium by sulphur dioxide. Barium tellurate $\text{BaTeO}_4 \cdot 3\text{H}_2\text{O}$ is fairly soluble in water.

Tellurium dissolves in warm concentrated (especially in fuming) sulphuric acid to a cherry-red solution, and from tellurium and sulphur trioxide the red solid STeO_3 (analogous to the blue S_2O_3 and green SSeO_3) is formed. When fused with potassium cyanide tellurium does not form a compound analogous to KCNS or KCNSe , but only the telluride K_2Te .

The atomic weight of tellurium.—The anomalous positions of iodine and tellurium in the periodic system led to the suspicion that tellurium might contain an unknown element of higher atomic weight.

Brauner (1889) attempted to separate this, and found that the atomic weight was considerably higher when tellurium was merely fused in an indifferent gas than when it was distilled in hydrogen. This has not been confirmed.

H. B. Baker and A. H. Bennett (1907) attempted to separate the supposed constituents : (1) by fractional crystallisation of telluric acid ; (2) by boiling barium tellurate with water (the solubility increases in the series $\text{BaSO}_4 \rightarrow \text{BaSeO}_4 \rightarrow \text{BaTeO}_4$) ; (3) by fractional distillation of Te , $\text{Te}(\text{C}_2\text{H}_5)_2$, TeCl_4 , and TeO_2 ; (4) by fractional electrolysis of tellurium compounds ;

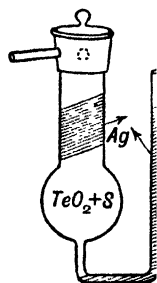


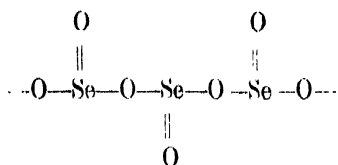
FIG. 270.—Atomic weight of tellurium.

(5) by fractional precipitation of TeCl_4 with water. The results were all negative. By heating TeO_2 with sulphur in a small tube (Fig. 270) the reaction $\text{TeO}_2 + \text{S} = \text{Te} + \text{SO}_2$ occurred, the excess of sulphur being kept back with silver foil. By this method, and the synthesis of TeBr_4 , the atomic weight $\text{Te} = 127.6$ was obtained, which is higher than the atomic weight of iodine, $\text{I} = 126.92$. Flint (1909) claimed to have separated fractions from tellurium by method (5), but this was not substantiated by Harcourt and Baker. Hönigschmid (1933), from the ratio $4\text{Ag} : \text{TeBr}_4$, found $\text{Te} = 127.59$. There are several isotopes of tellurium, but iodine is a simple element and has only one kind of atom. Hence the

average atomic weight of the mixture of tellurium isotopes is higher than the atomic weight of iodine.

Structures of selenium and tellurium compounds.—The gaseous compounds SF_6 , SeF_6 and TeF_6 contain molecules with the same octahedral structure (p. 461), the observed bond lengths being $\text{S}-\text{F}$ 1.57, $\text{Se}-\text{F}$ 1.68, and $\text{Te}-\text{F}$ 1.83, all much smaller than the calculated. The physical states of the dioxides SeO_2 and TeO_2 suggest at once a different structure from gaseous SO_2 , and this is confirmed by X-ray

examination. The selenium dioxide crystal contains long macromolecular zig-zag chains :



the angles being Se—O—Se 125° , —O—Se—O— 98° , —O—Se=O 90° . Tellurium dioxide has quite a different structure, the lattice being like that of brookite, one form of titanium dioxide TiO_2 , and since this is an ionic lattice the more metallic character of tellurium is in evidence. The ion TeO_6^{6-} of telluric acid has an octahedral structure like TeF_6 .

CHAPTER XXIX

NITROGEN

History.—In 1772 Daniel Rutherford allowed mice to breathe in air under a bell-jar and removed the fixed air (CO_2) by washing the residual gas with caustic potash solution. A gas remained which did not support combustion or respiration but, unlike fixed air, was not absorbed by alkali or lime-water. Priestley (1772) burnt charcoal in a confined volume of air and absorbed the fixed air with alkali, also obtaining a “mephitic air” which he called *phlogisticated air*. Both considered that the gas was common air saturated with *phlogiston* emitted by the animal or combustible body. Scheele (1772) proved that air is a mixture of two gases, *fire air* which supports combustion and respiration, and *foul air* which does not. Lavoisier (1775–6) gave a decisive proof of this, and called Scheele’s gas *azote* (Greek *a*, no; *zoe*, life), a name still used in France; the name nitrogen (Greek *nitron*, nitre) was suggested by Chaptal in 1790.

Atmospheric nitrogen was considered to be a pure substance until in 1894 Rayleigh and Ramsay found that it contains rather more than 1 per cent by weight of an inert gas which, unlike nitrogen, does not combine with heated magnesium. The inert gas, the existence of which had been indicated by Cavendish in 1785, was called **argon** (Greek *argon*, sluggish); later experiments by Ramsay and Travers showed that the atmosphere contains traces of other inert gases: **helium**, **neon**, **krypton** and **xenon**.

Occurrence.—Free nitrogen occurs in the atmosphere. The composition of air freed from moisture and carbon dioxide is roughly 4 volumes of nitrogen to 1 volume of oxygen; the exact figures (Leduc, 1896) are:

	By weight	By volume
Nitrogen - - -	75.5	78.06
Oxygen - - -	23.2	21.00
Argon, etc. - - -	1.3	0.94

The very nearly constant composition of dry atmospheric air was proved by Cavendish in 1783 (20.833 vols. of oxygen and 79.167 vols. of nitrogen and argon). Benedict (1912) and Carpenter (1937) found that the volume percentages of oxygen (20.939) and carbon dioxide (0.031) in uncontaminated air are very constant.

The atmosphere usually contains in addition to the above substances, minute quantities of carbon monoxide (in towns), hydrocarbons, hydrogen peroxide vapour, sulphur compounds such as hydrogen sulphide, sulphur dioxide and minute droplets of sulphuric acid, chlorides (especially near the sea), inorganic and organic dust, and moisture.

Traces of free nitrogen occur in volcanic gases and in gases evolved from coal; the gases from some springs may contain over 95 per cent of it by volume.

Nitrogen combined with hydrogen forms the base ammonia NH_3 , occurring in the free state and as salts in air, water, and volcanic products. In combination with oxygen, nitrogen forms nitrous acid HNO_2 and nitric acid HNO_3 . Extensive deposits of sodium nitrate occur in Chile. Animal and vegetable organisms contain complex organic substances called proteins, with an average of 16 per cent of nitrogen.

Preparation of nitrogen from air.—Nitrogen may be prepared: (a) from atmospheric air by removal of oxygen, (b) from nitrogen compounds. Atmospheric nitrogen is not quite pure since it contains about 1 per cent of inert gases, which give it a slightly higher density than pure nitrogen.

Oxygen is removed from air (previously freed from carbon dioxide) at the ordinary temperature by the action of phosphorus, moist iron filings, liver of sulphur, etc. Phosphorus, alkaline pyrogallol solution, acid chromous chloride solution, or a solution of cuprous chloride in hydrochloric acid or ammonia, remove atmospheric oxygen completely *on standing*: $4\text{CuCl} + 4\text{HCl} + \text{O}_2 = 4\text{CuCl}_2 + 2\text{H}_2\text{O}$. Metallic copper in contact with hydrochloric acid or ammonia may be used.

A long glass tube sealed at one end and fitted with a rubber stopper is divided into six equal volumes by labels. A solution of pyrogallol is poured in so as to occupy one division. A *small* piece of solid sodium hydroxide is slid into the upper part by means of crucible tongs, taking care that it does not fall into the liquid. The stopper is inserted and the tube shaken. The liquid becomes black owing to absorption of oxygen. The tube is opened under water: one of the remaining five divisions fills with water and four-fifths of the original volume of air remain as nitrogen.

Oxygen is removed from air by burning phosphorus, but not quite completely.

A porcelain capsule containing a piece of phosphorus is floated on water and covered with a stoppered bell-jar divided from the water level into five equal volumes by strips of waxed paper (Fig. 271). The phosphorus is kindled by a hot wire and the stopper is inserted. When the phosphorus ceases to burn the fumes of phosphorus pentoxide P_2O_5 dissolve in the water. When the apparatus has cooled the water levels are equalised. The residual gas occupies four volumes and extinguishes a lighted taper.

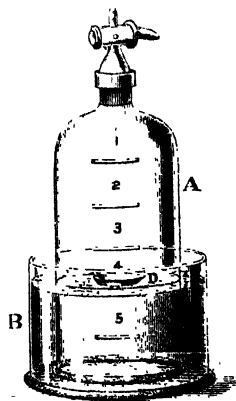
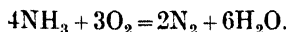


FIG. 271.—Burning phosphorus in air.

Oxygen is removed by *slowly* passing air, dried and freed from carbon dioxide by solid caustic potash, over a long length of clean copper turnings heated to *bright* redness in a hard-glass tube : $2\text{Cu} + \text{O}_2 = 2\text{CuO}$.

If air is bubbled through a warm concentrated solution of ammonia and the gas passed over a mixture of copper turnings and copper oxide heated to redness in a hard glass tube, the hydrogen of the ammonia is burnt by the oxygen of the air (Vernon Harcourt) :



The gas is a mixture of atmospheric and pure nitrogen, with a density intermediate between those of the two gases.

Nitrogen is made on the large scale either by passing air over red-hot copper, or mostly by the fractionation of liquid air (p. 149).

It should be noted that, as the boiling point of argon (-186°) is closer to that of oxygen (-183°) than to that of nitrogen (-196°), the nitrogen fraction contains very little argon ; it contains a little oxygen, which is separated when necessary in the laboratory by passing the commercial nitrogen over copper turnings heated to bright redness.

The volumetric composition of air.—The oxygen in a measured volume of air may be removed by absorbents and the contraction measured.

The most *accurate* method of finding the percentage by volume of oxygen in air is to explode a measured volume of air with excess of hydrogen. This may be done in a eudiometer over mercury (p. 42). The hydrogen unites with the oxygen to form water which condenses to a liquid of negligible volume, hence the volume of oxygen is found by taking *one-third* of the measured contraction.

A convenient apparatus for gas analysis is the Hempel gas burette and absorption pipette shown in Fig. 272.

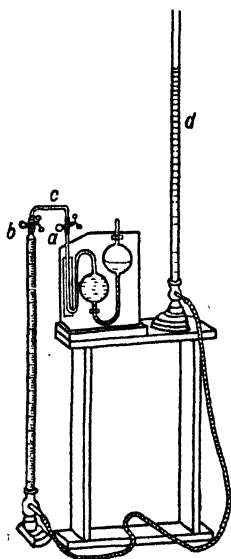


FIG. 272.—Hempel gas burette and pipette.

The burette and its levelling tube are mounted on two wooden stands weighted with lead and cut so that the two tubes may be brought close together. Connection with the pipette is made by glass capillary tube and rubber *pressure* tubing and the burette is closed with a spring clip. Burettes with glass taps are also obtainable but are more expensive. The burette and capillary tube are filled with water and the sample of gas from the pipette is drawn into the burette and measured, water from the pipette being passed over to fill the capillary tube. The pipette is then filled with a suitable absorbent, re-connected with the burette and the gas passed into the pipette. After shaking the

gas is passed back into the burette and measured. If necessary the burette and pipette containing the gas sample may be filled with mercury.

Suitable absorbents are concentrated potassium hydroxide solution for carbon dioxide or sulphur dioxide, alkaline pyrogallol for oxygen, ammoniacal cuprous chloride for carbon monoxide and acetylene, ferrous sulphate solution for nitric oxide, bromine water for ethylene.

If gases are to be exploded (*e.g.* a mixture of hydrogen and air or a hydrocarbon gas and oxygen), an **explosion pipette** (Fig. 273) fitted with platinum sparking wires is used, the gas being confined over mercury. The gas and oxygen are measured separately in the burette and passed into the explosion pipette, in which the mixture is sparked, the tap being closed and the pressure tubing on the pipette being closed by a strong screw clip and a piece of glass rod.

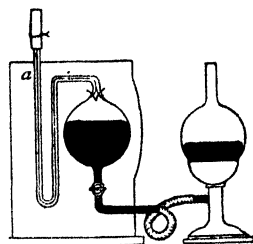


FIG. 273.—Explosion pipette.

The gravimetric composition of air.—The determination of the composition of air *by weight* is carried out by the method of Dumas and Boussingault (1841).

A long hard-glass tube *ab* packed with bright copper turnings and fitted with a stopcock at each end is evacuated and weighed, put in the furnace, and heated to bright redness. It is connected at one end with a large weighed vacuum globe *V* closed by a stopcock and at the other with a bulb

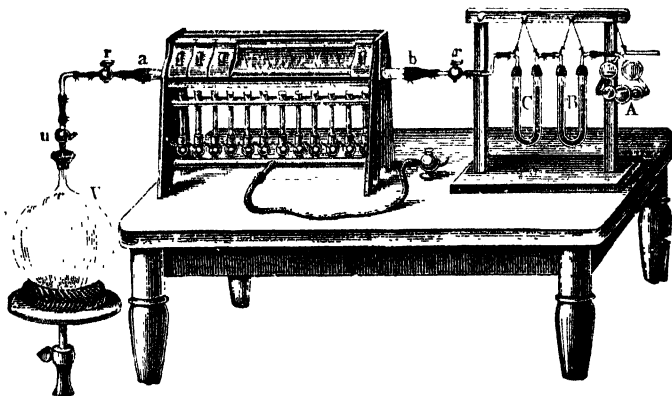


FIG. 274.—Gravimetric composition of air (Dumas and Boussingault's apparatus, modified).

of potassium hydroxide solution *A* and two U-tubes, one *B* containing solid potassium hydroxide and the other *C* (next to the tube containing the copper) calcium chloride, which remove carbon dioxide and moisture, respectively, from the air (Fig. 274).

The stopcocks are slightly opened and air is allowed to pass *slowly* over the heated copper, when the oxygen is absorbed to form copper oxide and

the nitrogen passes into the vacuous globe. When the globe is full of nitrogen the stopcocks are closed and the apparatus allowed to cool. The globe is weighed and thus the weight of the nitrogen found. The tube containing the copper and copper oxide is now weighed. The nitrogen in this tube is removed by a pump and the vacuous tube again weighed in order to find the weight of this nitrogen, which is added to that in the globe. The increase in weight of the *vacuous* tube gives the weight of oxygen. The nitrogen as weighed contains the argon and other inert gases. These can be determined by a separate experiment (see p. 961).

Dumas and Boussingault found that air contains 23.00 per cent of oxygen and 77.00 per cent of nitrogen (and argon), by weight.

Air is a mixture not a chemical compound.—That air is a mixture (really a *solution*) and not a compound of oxygen and nitrogen follows from the facts given below :

(i) Although the composition (when freed from water and carbon dioxide) is *nearly* constant it is not quite so, whereas every compound has a definite composition. The atomic ratio is also not simple but $N_{79}O_{21}$.

(ii) The constituents of air may be partly separated by diffusion (*atmolysis*) through a porous pipe-clay tube into a vacuum, when the nitrogen passes through more rapidly than the oxygen.

(iii) The constituents of air may be separated by the fractional distillation of liquid air.

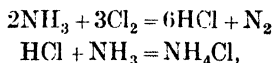
(iv) When air is shaken with water the dissolved part is richer in oxygen than the undissolved part.

(v) When oxygen and nitrogen are mixed there is no evolution or absorption of heat and all the properties of the mixture are intermediate between those of the constituents.

(vi) The relative density of air 14.4 ($H = 1$) corresponds with that of a mixture of *approximately* $4N_2 + O_2$; that of a compound N_4O would be 36.

Preparation of nitrogen from compounds.—Nitrogen is prepared in the laboratory by methods mostly depending on the oxidation of ammonia, the hydrogen being removed and the nitrogen set free.

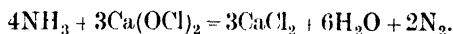
1. When chlorine gas is passed into, or bromine is added to, concentrated ammonia solution, nitrogen is evolved :



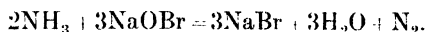
the reactions with bromine being similar.

In the case of chlorine the reaction is vigorous, flashes of light being seen in a darkened room ; care should be taken to keep the ammonia in excess otherwise the *very explosive* liquid nitrogen trichloride NCl_3 is formed (p. 525).

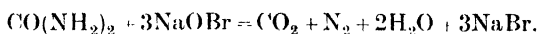
2. Instead of free chlorine a thin paste of 40 gm. of bleaching powder, containing calcium hypochlorite $\text{Ca}(\text{OCl})_2$, may be run through a thistle funnel into 100 ml. of concentrated ammonia solution warmed in a flask (explosions have been reported) :



Instead of bromine, sodium hypobromite solution (6 ml. of bromine freshly dissolved in a cold solution of 10 gm. of sodium hydroxide in 100 ml. of water) is dropped into concentrated ammonia solution :

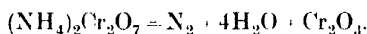


Nitrogen is also evolved by the action of alkaline hypobromite solution on urea :



This gas contains a trace of nitrous oxide N_2O , which is removed by passing over red-hot copper.

3. When red crystals of ammonium dichromate are gently heated they decompose violently with flashes of light, nitrogen and steam are evolved and a voluminous green residue of chromic oxide is left :



4. The most convenient method of preparing nitrogen is to heat a solution containing ammonium nitrite, made by dissolving equimolecular amounts of sodium nitrite and ammonium chloride or sulphate in water :



The gas evolved is washed with dilute sulphuric acid to remove ammonia, and collected over water.

The reaction may become violent and the liquid froth considerably. A little potassium dichromate may be added to the reaction mixture to prevent the formation of nitric oxide. Since the reaction is stopped by making the solution just alkaline with ammonia, it is probable that free nitrous acid is the active agent.

30 gm. of sodium nitrite dissolved in the smallest amount of cold water is mixed with a cold saturated solution of 22 gm. of ammonium chloride, and the liquid filtered. Two lots of a mixture of 5 ml. of the solution and 20 ml. of water are made ; one (A) is made faintly alkaline by a drop or two of 0.880 ammonia and the other (B) is made faintly acid by a drop or two of dilute sulphuric acid. The two solutions are heated in small flasks on a hot plate : solution A may be heated to boiling without appreciable decomposition, whilst B evolves nitrogen freely.

The main quantity of the mixed solutions of sodium nitrite and ammonium chloride is diluted with an equal volume of water and heated in a flask for the preparation of nitrogen.

5. Pure nitrogen is obtained by passing a mixture of nitric oxide and ammonia gas over red-hot copper :

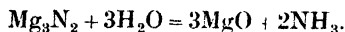


6. Very pure nitrogen is evolved on heating barium azide in an evacuated apparatus : $\text{Ba}(\text{N}_3)_2 = \text{Ba} + 3\text{N}_2$. (This preparation does not involve an oxidation of ammonia).

Nitrogen gas may be dried by calcium chloride, concentrated sulphuric acid or phosphorus pentoxide, and collected over mercury. Compressed nitrogen in grey cylinders may be bought : it usually contains a little oxygen, which may be taken out by passing over copper turnings heated to *bright* redness.

Properties of nitrogen.—Nitrogen is a colourless, odourless, tasteless gas, normal density 1.2507 gm./lit. (atmospheric nitrogen is 0.48 per cent heavier) : it does not support combustion or respiration, although it is not poisonous : it does not turn lime-water milky. It is sparingly soluble in water and has no action on litmus. It is liquefied by strong cooling ; critical temperature -147.13° , critical pressure 33.49 atm. The liquid is colourless, b. pt. -195.81° , density at b. pt. 0.8042, and on rapid evaporation under reduced pressure it forms a colourless ice-like solid, m. pt. $-210.5^\circ/86$ mm.

Nitrogen is an inert element, since the heat of dissociation of the molecule is very large, but it combines directly with hydrogen and oxygen on sparking, with lithium slowly at room temperature to form the nitride Li_3N (more rapidly on heating), and with magnesium, calcium, strontium and barium at a red heat to form the nitrides M_3N_2 . (It should be noted that sodium and potassium do *not* form nitrides in this way). Boron and aluminium form BN and AlN at a bright red heat ; silicon forms Si_3N_4 only at a white heat. Nitrides of many metals are formed by heating the finely divided metal, or a salt, in ammonia gas. Lithium nitride is decomposed by cold water, nitrides of alkaline earth elements by hot water, boron and aluminium nitrides on heating in steam. Ammonia and the oxide or hydroxide of the other element are formed :



The formation of magnesium nitride may be shown by heating with a blowpipe flame some magnesium powder in nitrogen in the short limb of a bent *hard* glass tube over mercury. The mercury slowly rises owing to absorption of nitrogen.

Active nitrogen.—An active form of nitrogen is obtained by subjecting a current of nitrogen, drawn through a tube at 2 mm. pressure, to a high tension discharge with a condenser in circuit (Fig. 275). The gas travelling beyond the discharge glows with a yellow light. Active nitrogen was discovered by Lord Rayleigh in 1911. A trace of oxygen, mercury vapour,

etc., is necessary in its production, although an excess destroys it. It is without action on molecular oxygen or hydrogen, but with acetylene it yields hydrocyanic acid. White phosphorus is converted into red phosphorus, and sodium and mercury form compounds at 150° , when exposed to the gas. Nitric oxide is decomposed into nitrogen and oxygen.

Lord Rayleigh supposed that active nitrogen is atomic nitrogen. (Glowing nitrogen probably contains several varieties of the element, including the normal atom and atoms and molecules with various additional amounts of energy as compared with the normal unexcited states. Pieces of gold, silver, copper, or platinum become red-hot and even melt, when exposed to active nitrogen, without any chemical action on the metal. Debeau (1942) found that the pressure of an enclosed volume of nitrogen at 0.5 mm. pressure rose to nearly twice the initial value when the gas was subjected to an electrodeless discharge, indicating nearly complete dissociation of N_2 into atoms. The chemical activity seems to be due to the atomic forms, and the production of the glow to collisions between various types of nitrogen atoms and molecules. The effect of traces of impurities (optimum about 0.1 per cent) in the production of the glow is attributed to their adsorption on the walls of the vessel, thus preventing recombination of nitrogen atoms by collision with the surface. In a flask coated with metaphosphoric acid the glow persists for several hours.

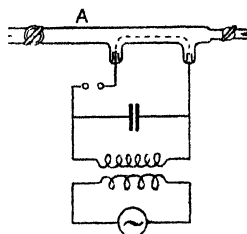


FIG. 275.—Production of active nitrogen.

Compounds of nitrogen and hydrogen.—Nitrogen forms three well-defined compounds with hydrogen: ammonia NH_3 , hydrazine N_2H_4 , and hydrazoic acid N_3H .

Ammonia and hydrazine are *basic substances*, combining with acids to form ammonium and hydrazine salts: e.g., $NH_3 \cdot HCl$ or NH_4Cl , $N_2H_4 \cdot HCl$ or N_2H_5Cl , and $N_2H_4 \cdot 2HCl$ or $N_2H_6Cl_2$. Part of the hydrogen of ammonia and hydrazine may, however, be replaced by alkali metals, forming e.g. $NaNH_2$ and $H_2N \cdot NHNa$. Hydrazoic acid is an *acid*, dissolving metals and forming salts, e.g. NaN_3 . It combines with ammonia and with hydrazine to form the compounds NH_4N_3 (or N_4H_4) and $N_2H_5N_3$ (or N_5H_5), respectively. The ion N_3^- is univalent.

AMMONIA

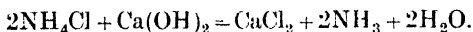
History.—Ammonium chloride NH_4Cl , called *sal ammoniac*, appears to have been obtained in the Middle Ages from volcanoes in Central Asia, or prepared in Egypt from the soot formed on burning camels' dung. Gaseous ammonia was obtained by Priestley in 1774 by collecting over mercury; he called it *alkaline air* and found that when sparked it increases in volume and a combustible gas is formed. Berthollet in 1785 showed that nitrogen and hydrogen were formed in

this decomposition: $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$; the result was confirmed by Austin (1788), and the formula NH_3 was established by Davy (1800) and Henry (1809).

Occurrence.—Traces of ammonia occur in the atmosphere: bottles containing hydrochloric acid become coated after a time with ammonium chloride. Ammonium chloride NH_4Cl , and sulphate $(\text{NH}_4)_2\text{SO}_4$, occur in volcanic districts; ammonia accompanies boric acid in the *soffioni* of Tuscany (p. 653). Small quantities of ammonium salts occur in plants and animals (*e.g.* in blood and in urine), in rock salt, in the soil, and in natural waters (as nitrite and nitrate).

Preparation.—Ammonia is formed from its elements when these are sparked together: $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ (Regnault, 1840). Deville (1864) pointed out that electric sparks both form and decompose ammonia. The reaction is reversible and a state of equilibrium is set up in which 6 per cent of NH_3 exists with 94 per cent of the uncombined gases. If the mixture $\text{N}_2 + 3\text{H}_2$ and pure ammonia, respectively, are exposed in eudiometers to prolonged sparking, contraction ensues in the first case and expansion in the second until the volumes and compositions are the same. Ammonia is also formed when a mixture of nitrogen and hydrogen is exposed to the silent electric discharge.

In the laboratory ammonia gas is prepared by heating ammonium chloride with dry slaked lime:



A mixture of 50 gm. of powdered ammonium chloride with 150 gm. of powdered slaked lime ground in a mortar, is transferred to a 250 c.c. flask, which is then filled with small lumps of quicklime. A cork and delivery tube leading to a drying tower filled with lumps of quicklime are fitted and

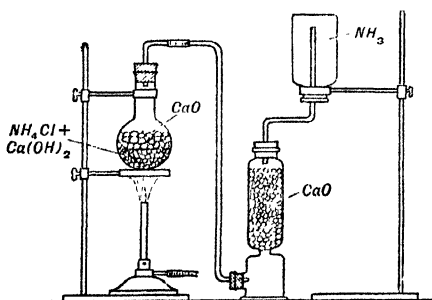
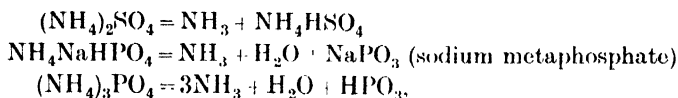


FIG. 276.—Preparation of ammonia gas.

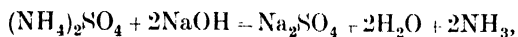
the flask is heated on wire gauze. The gas is collected by upward displacement as it is lighter than air (Fig. 276). The jar is full when a piece of moist red litmus paper held near the mouth is turned strongly blue. Concentrated sulphuric acid reacts violently with the gas forming ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, and calcium chloride absorbs it forming a compound $\text{CaCl}_2 \cdot 8\text{NH}_3$, hence these reagents cannot be used to dry ammonia.

Quicklime or pieces of potassium or sodium hydroxide may be used. Phosphorus pentoxide reacts with ammonia gas unless it is already very dry and pure.

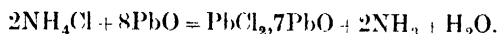
Ammonia is evolved on heating ammonium sulphate, microcosmic salt, or ammonium phosphate :



but these are not convenient methods of preparation. It is also formed when ammonium salts are heated with a solution of sodium hydroxide :

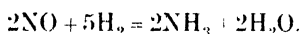


or when ammonium chloride is heated with litharge, when an oxychloride of lead $\text{PbCl}_2 \cdot 7\text{PbO}$ remains :



A convenient method of obtaining ammonia gas in small quantities is to warm the concentrated aqueous solution (*liquor ammoniac fortis*, sp. gr. 0.880) in a flask; the gas is dried with quicklime. This is not of course strictly speaking a *preparation* of ammonia.

Ammonia is formed by the reduction of some oxygen compounds of nitrogen. A mixture of hydrogen and nitric oxide, a higher oxide of nitrogen (but not nitrous oxide) or even nitric acid vapour, passed over heated platinum, is reduced to ammonia :



Reduction may be effected by nascent hydrogen. Dilute nitric acid in presence of dilute sulphuric acid is reduced by zinc to ammonium sulphate : $\text{HNO}_3 + 8\text{H} = \text{NH}_3 + 3\text{H}_2\text{O}$. Sodium nitrate, or more readily sodium nitrite, is reduced by zinc and hot sodium hydroxide solution, giving pure ammonia. Aluminium may be used instead of zinc, but nitrates are most easily reduced in alkaline solution by powdered Devarda's alloy, containing 45 parts of aluminium, 50 of copper and 5 of zinc. This method is used for the determination of nitrates or nitrites, the ammonia being distilled into standard acid.

Ammonia is evolved on heating organic matter containing nitrogen (horn, bones, etc.) with *soda-lime* (prepared by slaking quicklime with sodium hydroxide solution and heating till dry), and ammonium sulphate is formed when organic matter containing nitrogen is heated for some time with concentrated sulphuric acid (*Kjeldahl's method* for the determination of nitrogen).

Properties.—Ammonia is a colourless gas lighter than air, normal density 0.7708 gm./lit. (Moles, 1934, found 0.7714), and fairly easily liquefied by cold or pressure, forming a colourless liquid, b. pt. -33.4° , freezing at a low temperature to an ice-like solid, m. pt. -77.7° . The critical temperature is 132.5° , the critical pressure 112.3 atm. The liquid may be obtained by cooling with a mixture of ice and crystalline

calcium chloride : it is produced on a large scale by compressing the gas into steel coils cooled with water and is sent out in steel cylinders as *anhydrous ammonia*. The gas has a characteristic pungent smell, and is readily soluble in water (1148 vols. in 1 vol. of water at 0° and 739 at 20°). The solubility of ammonia in water obeys Henry's law only above 100° : all the gas is expelled on boiling a solution.

The solubility of ammonia gas may be demonstrated by the " fountain " experiment (Fig. 125), red litmus solution being used, which is turned blue by the ammonia, which is alkaline.

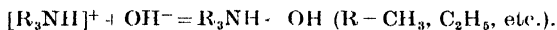
The aqueous solution of ammonia is prepared by passing the gas into cold distilled water : the flask must be kept cool by running water over the outside since a considerable amount of heat is evolved. The liquid also expands considerably.

Specific gravities D_{15}^{15} of aqueous ammonia at 15.5°.

Sp. gr.	%NH ₃	Sp. gr.	%NH ₃
0.875	36.90	0.950	12.74
0.880	35.20	0.960	9.95
0.890	31.85	0.970	7.27
0.900	28.50	0.980	4.73
0.910	25.15	0.990	2.31
0.920	21.85	0.992	1.84
0.930	18.69	0.996	0.91
0.940	15.65	0.998	0.45

The aqueous solution is alkaline : $\text{NH}_3 + \text{H}^+ + \text{OH}^- = \text{NH}_4^+ + \text{OH}^-$. By strong cooling, the crystalline hydrates $\text{NH}_3 \cdot \text{H}_2\text{O}$ (m. pt. - 79.0°) and $2\text{NH}_3 \cdot \text{H}_2\text{O}$ (m. pt. - 78.9°) are obtained. A crystalline compound $\text{NH}_3 \cdot \text{H}_2\text{O}_2$ is formed by the action of ammonia on cold concentrated hydrogen peroxide.

It has been supposed that ammonia solutions contain ammonium hydroxide, NH_4OH , a weak base of the same strength as acetic acid (p. 300), together with free NH_3 ; $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$. The weakness of NH_4OH (also of amines) may be due to removal of OH^- ions, by the lone pair of electrons on the oxygen forming a covalent link with the hydrogen attached to nitrogen :



Quaternary ammonium hydroxides, with no H attached to N, cannot form such covalent compounds and are powerful bases : $[\text{R}_4\text{N}]^+ + \text{OH}^-$.

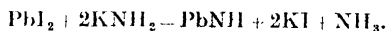
Ammonia is soluble in alcohol : 1 litre of alcohol dissolves 130 gm. of NH_3 at 0°.

If ammonia gas is passed over heated potassium or sodium, one-third of the hydrogen is replaced by the metal, and **potassamide** KNH_2 , or **sodamide** NaNH_2 , is formed. These are white solids when pure. They contain the univalent amino group, $-\text{NH}_2$.

Pass ammonia, dried over quicklime or caustic soda, over a piece of potassium heated in a hard-glass bulb tube. The metal boils, emitting a green vapour, and reaction then begins. The hydrogen evolved may be kindled at the end of the tube, and a brown mass of impure potassamide is left in the tube: $2K + 2NH_3 = 2KNH_2 + H_2$.

The alkali metal amides are violently decomposed by water, with evolution of ammonia: $NaNH_2 + HOH = NaOH + NH_3$.

The bivalent imino-group $=NH$ is known in organic compounds and in the orange-red solid explosive lead imide, $PbNH$, formed from potassamide and lead iodide in liquid ammonia:

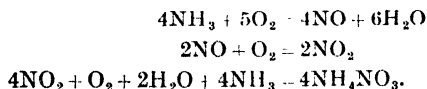


Ammonia is not combustible in air and does not support combustion, but the flame of a taper before it is extinguished in the gas is surrounded by a large greenish-yellow flame, due to decomposition of ammonia by heat: $2NH_3 = N_2 + 3H_2$, and combustion of the hydrogen. Ammonia gas burns in oxygen with a greenish-yellow flame, and a mixture of ammonia and oxygen explodes when kindled: $4NH_3 + 3O_2 = 6H_2O + 2N_2$.

Pass a current of ammonia through a tube surrounded by a wider tube through which oxygen is passing (Fig. 277). If a lighted taper is held over the tubes, the ammonia burns with a large, three-coned, yellowish flame.

In contact with heated platinum, a mixture of ammonia gas and air or oxygen is catalytically oxidised to nitric oxide.

Pass oxygen through a little concentrated ammonia warmed in a 200 ml. conical flask, and suspend a red-hot spiral of platinum wire in the flask. The mixture of ammonia and oxygen explodes feebly: $4NH_3 + 3O_2 = 6H_2O + 2N_2$. The wire cools owing to combustion ceasing, but after a short time the wire again becomes red-hot, and there is another explosion when the gas mixture is renewed. During oxidation without explosion, red oxides of nitrogen and white fumes of ammonium nitrate are formed:



A jet of oxygen can be made to burn under the surface of the ammonia solution.

According to Schlumberger and Piotrowski (1914) mixtures with air containing 16.5 to 26.8 per cent ammonia can be exploded by an electric spark in a spherical glass vessel. Berl and Bausch (1929) found that only the mixture with 21.9 per cent ammonia ($4NH_3 + 3O_2$) can be exploded by

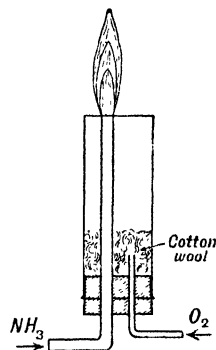
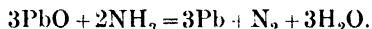


FIG. 277.— Combustion of ammonia in oxygen.

a heated silver wire in a metal container at atmospheric pressure : at higher pressures, mixtures on both sides of this composition are explosive.

Ammonia gas may be detected (1) by its smell, (2) by the blueing of moist red litmus paper, (3) by the white fumes of ammonium chloride formed around a glass rod dipped in concentrated hydrochloric acid, (4) by blackening a piece of paper dipped in mercurous nitrate solution.

Ammonia gas reduces many heated oxides of metals (*e.g.* CuO, PbO ; with copper oxide some nitric oxide is also formed, see p. 519).



Ammonia is readily absorbed by calcium to form $\text{Ca}(\text{NH}_3)_6$ and by dry silver chloride forming the compounds $\text{Ag}(1,3\text{NH}_3)$ and $2\text{AgCl}, 3\text{NH}_3$. If the silver compound in one limb of a bent sealed tube is gently heated, liquid ammonia collects in the other limb immersed in a freezing mixture. On allowing the silver chloride to cool the ammonia is reabsorbed. Ammonia forms compounds with many other metal salts : these usually decompose easily on warming, evolving ammonia.

Ammonia is not easily decomposed by heat, especially if diluted with an indifferent gas. It is decomposed by ultra-violet light and by radium emanation.

The composition of ammonia.—On *prolonged* sparking of ammonia gas in a eudiometer it is decomposed into nitrogen and hydrogen, and the volume is nearly doubled (a little ammonia remains undecomposed, see page 514). If oxygen is now added and a spark passed, or if the mixture is passed over palladium at 200° , water is formed and two-thirds of the contraction is equal to the volume of the hydrogen. (The composition of ammonia cannot be determined by exploding the gas with oxygen, since part of the nitrogen, up to 16 per cent, is also oxidised.)

Twenty c.c. of ammonia expanded to 40 c.c. on sparking. Oxygen was added till the volume was 157 c.c. After passing a spark the volume was 112 c.c. \therefore contraction on explosion with oxygen = 45 \therefore volume of hydrogen = $\frac{2}{3} \times 45 = 30$ \therefore volume of nitrogen = $40 - 30 = 10$. Thus 1 vol. of nitrogen + 3 vols. of hydrogen = 2 vols. of ammonia.

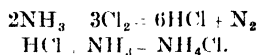
From Avogadro's hypothesis, it follows that 1 molecule of nitrogen and 3 molecules of hydrogen form 2 molecules of ammonia. Hence 1 molecule of ammonia contains $\frac{1}{2}$ a molecule (1 atom) of nitrogen* and $\frac{3}{2}$ molecules (3 atoms) of hydrogen, and the formula is NH_3 . This may be *confirmed* by the density of the gas, which shows that the molecular weight is 17.

* The ratio of specific heats of nitrogen and of hydrogen, c_p/c_v , is 1.40, the value for a diatomic gas, and if the atomic weights are known the densities lead to the formulæ H_2 and N_2 .

On electrolysis of a mixture of 10 vols. of saturated sodium chloride solution and 1 vol. of concentrated (sp. gr. 0.880) ammonia solution, 1 vol. of nitrogen gas is evolved from the anode and 3 vols. of hydrogen from the cathode.

The *volumetric composition* of ammonia may be demonstrated by *Hofmann's experiment*.

A long tube (Fig. 278) is divided below the stopcock into three equal volumes by rubber bands and is filled with dry chlorine. The tube above the stopcock is one-third filled with concentrated ammonia solution, which is cautiously added in small portions to the chlorine, the tube being cooled by water. Each addition of ammonia reacts with a yellowish-green flame and the formation of white clouds of ammonium chloride

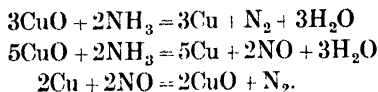


The fumes are washed down by shaking and dilute sulphuric acid is added to fix the excess of ammonia.

The tube is cooled by immersing in a large cylinder of water and the upper part above the tap is fitted with a cork and siphon tube dipping into water, the whole being filled with water. On opening the tap water runs into the long tube and it is found that the residual nitrogen occupies 1 vol.

The 3 vols. of chlorine have combined with 3 vols. of hydrogen from the ammonia to form HCl, ∴ 1 vol. of nitrogen is combined in ammonia with 3 vols. of hydrogen. Hence the formula is $(\text{NH}_3)_x$. In this case a density determination is required to show that $x = 1$.

In the *gravimetric analysis* a measured volume of dry ammonia gas, the weight of which under the given conditions may be calculated from the density, is passed slowly through a hard glass tube containing red-hot copper oxide followed by copper turnings heated to bright-redness to reduce oxides of nitrogen :



The water formed is collected in weighed calcium chloride tubes and the weight of hydrogen calculated. The nitrogen passing on is collected in a weighed exhausted globe. In this way the weight ratio N : H is found to be 14 : 3. This is in the ratio of 1 atom of nitrogen to 3

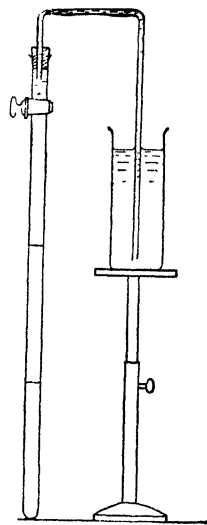


FIG. 278.—Volumetric composition of ammonia

atoms of hydrogen, hence the formula is $(\text{NH}_3)_x$. The volume of nitrogen collected occupies *half* the volume of the ammonia taken (pressure and temperature being the same), hence $x=1$. The formula is *confirmed* by a density determination. (The apparatus of Fig. 274 may be adapted to this experiment.)

The manufacture of ammonia.—Ammonia (and ammonium salts) are made on the large scale by three processes.

1. From the *ammoniacal liquor* obtained as a by-product in the manufacture of coal gas or the carbonisation of coal in recovery coke-ovens.

Most of the ammonia is now made from atmospheric nitrogen :

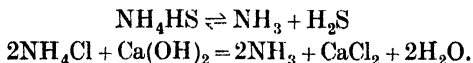
2. by the *cyanamide process*,

3. by direct *synthesis* from nitrogen and hydrogen. This is the most important method.

By-product ammonia.—Ammonium salts, especially ammonium sulphate, are recovered as by-products in the manufacture of gas or coke from coal. Bituminous coal contains about 1 per cent of combined nitrogen, part of which is recovered in carbonisation, mainly as ammonia although a little hydrocyanic acid, HCN, is present. The average yield of ammonia in gas-works and coke-ovens is 20–25 lb. of ammonium sulphate per ton of coal, less than 20 per cent of the nitrogen in the coal. Most of the nitrogen remains in the coke, and a total recovery of 60 per cent of the nitrogen in the fuel may be obtained by carbonising in a current of steam or by blowing steam through the coke.

Ammoniacal liquor contains tar and organic compounds, free ammonia, and ammonium salts of two kinds : (1) *Volatile*, decomposed by boiling alone, e.g. ammonium carbonates, sulphide and hydrosulphide, cyanide, and acetate(?); (2) *Fixed*, not decomposed by boiling but decomposed by lime, e.g. ammonium sulphate, sulphite, thiosulphate, thiocarbonate, chloride, thiocyanate, and ferrocyanide. The total ammonia may be about 17 gm. per litre.

The ammonia is recovered by means of **ammonia stills**, in which the liquor is heated by steam to drive out the free and volatile ammonia, and the residue is then treated with milk of lime and additional steam to decompose the fixed salts :



A typical still is shown in Fig. 279. It consists of an iron column containing perforated plates, the holes being covered with caps. In the upper part the ammoniacal liquor is treated with steam passed in at the base, and ascending through the column to drive out the volatile ammonia; most of the steam is condensed in the upper part. Milk of lime is added in the middle part, and the sludge allowed to pass out at the base. The ammonia set free by the lime is driven out by the steam.

The ammonia is bubbled into 60 per cent sulphuric acid in a lead-lined tank, when crystals of ammonium sulphate separate; these after draining contain 93-99 per cent of $(\text{NH}_4)_2\text{SO}_4$ with a little tarry matter and free acid. If the ammonia gas is passed through a washer containing milk of lime to remove hydrogen sulphide, and then through charcoal or a heavy oil washer to remove tarry matter, it may be dissolved in water to form a solution. Usually "25 per cent liquor" is made; the special strong liquor of density 0.880 (35 per cent NH_3) requires very careful cooling in its preparation. The ammonium sulphate is nearly all used in agriculture as a fertiliser.

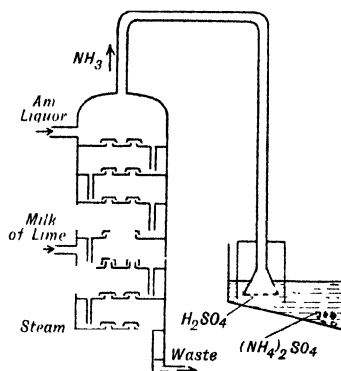
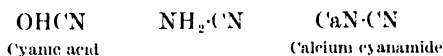


FIG. 279.- Ammonia still.

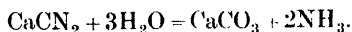
Attempts have been made to recover ammonia from crude coal gas by passing it through sulphuric acid without previous deposition of ammoniacal liquor. This direct process is worked in connection with coke-ovens.

The cyanamide process.—In this process nitrogen gas is passed over crushed calcium carbide, heated at 1100° by carbon rods heated electrically inside drums of carbide, or by raking the carbide mixed with some calcium chloride or fluoride continuously through a furnace heated with electric arcs. Calcium cyanamide mixed with graphite is formed as a dark grey mass called "cyanamide" or "nitrolim": $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$.

Calcium cyanamide is a derivative of cyanamide, the amide of cyanic acid (*i.e.* cyanic acid in which hydroxyl is replaced by the amino-group):



When calcium cyanamide is heated with water under pressure, calcium carbonate and ammonia are formed:



The "cyanamide" is agitated with cold water to remove unchanged carbide, and then stirred with water and a little sodium carbonate in large iron autoclaves (*i.e.* pressure digesters) into which steam is blown until the pressure rises to 3-4 atm. The pressure then rises automatically to 12-14 atm. owing to production of ammonia, which is blown off with some steam through condensers, the solution formed being heated in a still with steam to drive out the ammonia gas.

Finely-ground "cyanamide" is also used directly as a fertiliser, decomposition with formation of ammonium salts taking place in the soil. Calcium cyanide is produced by fusing "cyanamide" alone or mixed with common salt in an electric furnace: $\text{CaCN}_2 + \text{C} = \text{Ca}(\text{CN})_2$. By the action of dilute sulphuric acid on "cyanamide" urea is formed: $\text{NC}\cdot\text{NH}_2 + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$.

Synthetic ammonia.—The direct combination of nitrogen and hydrogen is used on the technical scale in the **Haber process** (1905) for the synthetic production of ammonia. Since the volume decreases in the reaction: $N_2 + 3H_2 = 2NH_3$, the amount of ammonia formed in equilibrium will increase with the pressure. Heat is evolved in the reaction, hence the amount of ammonia in equilibrium will decrease with rise of temperature.

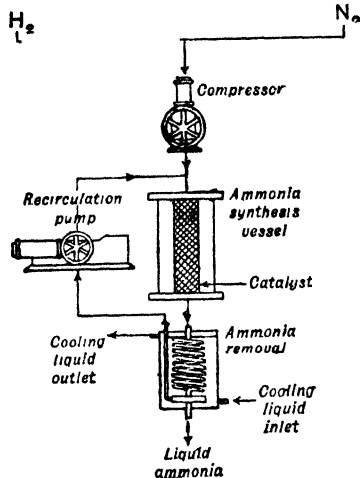


FIG. 280.—Synthetic ammonia apparatus (diagrammatic).

The mixture of nitrogen and hydrogen, which must be very pure, is circulated by pumps under 100–200 atm., or 1000 atm. pressure in Claude's process, over a heated catalyst (500°), which may be iron with "promoters," usually aluminium oxide and potassium oxide. The ammonia formed in each circulation is removed by cooling and liquefaction under pressure, or by absorption in water. The argon in the atmospheric nitrogen is blown off from time to time with some of the mixture of nitrogen and hydrogen. The percentages of ammonia

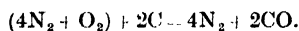
by volume present *in equilibrium* at various temperatures and pressures are given in the table below.

When the plant is working at an economical rate, the gas does not remain in contact with the catalyst long enough to allow equilibrium to be reached, so that the conversions are smaller than these. The same considerations as to the effect of temperature on equilibrium and reaction velocity apply here as in the case of the manufacture of sulphur trioxide (p. 471).

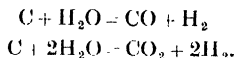
	10	100	300	1000 atm. pressure.
400° C.	3.85	25	47	80
450	2.1	16.5	36	70
500	1.2	10.6	26.4	57.5
550	0.76	6.8	19	41
600	0.5	4.5	14	31.5
700	0.23	2.2	7.3	13

The hydrogen is prepared electrolytically, or from water gas or by liquefying the more condensable gases in coke-oven gas (p. 164). The nitrogen is obtained from air by liquefaction and fractionation. A mixture of $N_2 + 3H_2$ is also made directly from a mixture of producer gas, water gas, and steam by passing over a catalyst.

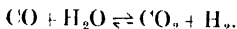
The producer gas is mainly a mixture of carbon monoxide and nitrogen formed by passing air through a mass of red-hot coke :



Water gas is a mixture of hydrogen, carbon monoxide, and carbon dioxide, formed by passing steam through a mass of red-hot coke :

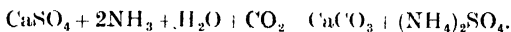


A suitable mixture of producer gas, water gas, and steam is passed over a heated catalyst consisting of ferric oxide with promoters (chromic oxide, etc.), when the carbon monoxide is nearly all removed by the reaction :



The carbon dioxide and residual carbon monoxide are removed from the gas as described on p. 165, and the dry purified mixture of $\text{N}_2 + 3\text{H}_2$ is compressed and passed to the ammonia synthesis apparatus.

The catalyst vessels are of chrome steel (hydrogen permeates heated carbon steel), internally heated by electricity. The ammonia may be liquefied for use in refrigeration plant, or dissolved in water, or converted into ammonium sulphate by the calcium sulphate process, in which ammonia gas is dissolved in a suspension of anhydrite (CaSO_4) in water, and carbon dioxide is passed in :



The solution of ammonium sulphate is filtered from the calcium carbonate and evaporated. Crystallised ammonium chloride is made from synthetic ammonia by the ammonia-soda process (p. 691).

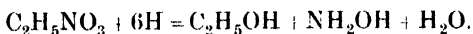
Hydroxylamine.—Hydroxylamine NH_2OH was discovered by Lossen in 1865. Its salts may be regarded as ammonium salts in which the ammonium radical NH_4 is replaced by the hydroxylaminium radical $\text{NH}_3(\text{OH})$. They are often formulated as addition compounds of hydroxylamine and the acid, *e.g.* $\text{NH}_2\text{OH} \cdot \text{HCl}$ instead of $\text{NH}_3(\text{OH})\text{Cl}$. Salts of hydroxylamine are obtained by :

1. The reduction of nitric oxide with nascent hydrogen :



Nitric oxide is passed through flasks containing granulated tin and concentrated hydrochloric acid. Reduction occurs to **hydroxylamine hydrochloride** $\text{NH}_2\text{OH} \cdot \text{HCl}$ (or **hydroxylaminium chloride** $\text{NH}_3(\text{OH})\text{Cl}$) and ammonium chloride NH_4Cl . According to Divers, an ammonium salt is not formed in complete absence of air. The solution is treated with hydrogen sulphide to precipitate tin as sulphides, filtered, and evaporated to dryness. The residue is extracted first with cold and then with boiling absolute alcohol, which dissolves the hydroxylamine but not the ammonium salt. Hydroxylamine hydrochloride is then precipitated from the alcoholic solution by ether.

2. The reduction of ethyl nitrate by nascent hydrogen :



Thirty gm. of $\text{C}_2\text{H}_5\text{NO}_3$, 120 gm. of granulated tin, and 40 gm. of HCl (sp. gr. 1.12) are mixed, when reaction occurs spontaneously. The solution is treated as in (1).

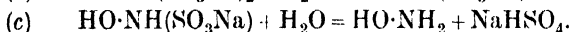
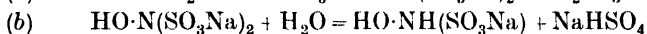
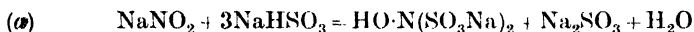
3. The electrolytic reduction of nitric acid (Tafel, 1902) :



A cooled lead anode is separated by a porous pot from an amalgamated lead beaker serving as a cathode, the whole being cooled by ice. Fifty per cent sulphuric acid is placed in each compartment, and 50 per cent nitric acid added drop by drop to the cathode compartment. Hydroxylamine sulphate $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ is formed. By precipitating a solution of this with barium chloride, hydroxylamine hydrochloride is formed :

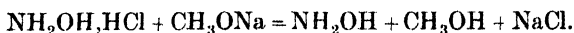


4. The interaction of nitrites and acid sulphites in solution (Raschig, 1887). The reaction occurs in three stages. If the hydrogen in the NH_2 group in hydroxylamine is replaced by the group SO_3H or $\text{H}\cdot\text{SO}_2\cdot\text{O}$ —, which is the radical of the sulphonic acid form of sulphurous acid (p. 469) $\text{H}\cdot\text{SO}_2\cdot\text{OH}$, then hydroxylamine monosulphonic acid $\text{NH}(\text{SO}_3\text{H})\cdot\text{OH}$ and hydroxylamine disulphonic acid $\text{N}(\text{SO}_3\text{H})_2\cdot\text{OH}$ are formed. In the reaction sodium hydroxylamine disulphonate is first formed, and this is then hydrolysed with the formation of sodium hydroxylamine monosulphonate and then hydroxylamine :



Sulphur dioxide is *slowly* passed into a concentrated solution of 2 mols of commercial NaNO_2 and 1 mol of Na_2CO_3 at -2° , with good stirring, until just acid. The solution, containing sodium hydroxylamine disulphonate, is warmed with a few drops of dilute sulphuric acid, when hydrolysis to sodium hydroxylamine monosulphonate occurs. It is then kept at 90° – 95° for two days, when hydrolysis to hydroxylaminium sulphate $(\text{NH}_3\text{OH})_2\text{SO}_4$ occurs. It is neutralised with sodium carbonate, evaporated to small bulk, and cooled, when Glauber's salt $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ crystallises. The filtrate on further evaporation deposits hydroxylaminium sulphate, which is quickly recrystallised from water.

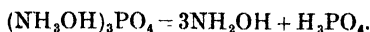
Anhydrous hydroxylamine was prepared by Lobry de Bruyn (1891) by adding a solution of sodium methoxide in methyl alcohol (obtained by dissolving sodium in the alcohol) to a solution of hydroxylamine hydrochloride in methyl alcohol, filtering off the sodium chloride, and distilling under reduced pressure (40 mm.), when methyl alcohol first distils and then hydroxylamine :



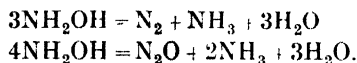
It also crystallises on cooling the filtered solution to -18° (Lecher and Hofmann, 1922).

Crismer (1890) prepared the compound of hydroxylamine with zinc chloride $\text{ZnCl}_2\cdot 2\text{NH}_2\text{OH}$ by boiling zinc oxide with hydroxylaminium chloride solution and distilled it at 120° , either alone or mixed with

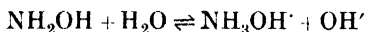
aniline. Uhlenhuth (1900) heated hydroxylaminium phosphate at 135° under 13 mm. pressure :



Pure hydroxylamine forms colourless, odourless, very deliquescent scales or hard rhombic needles, sp. gr. 1.35, m.pt. 33°. It may be distilled under reduced pressure (55°–58°/22 mm.) but explodes when heated at ordinary pressure. The vapour explodes at 60°–70° in contact with air. The vapour density corresponds with the formula NH_2OH . The solid slowly decomposes above 15°, evolving nitrogen, ammonia, and nitrous oxide ; solutions containing up to 60 per cent of hydroxylamine also slowly decompose :

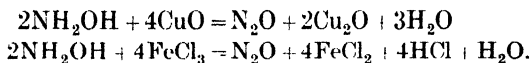


The solution is a weaker base than ammonia :

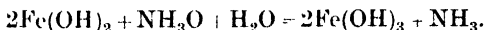


and precipitates hydroxides of many metals (Al, Zn, etc.). The salts are hydrolysed in solution.

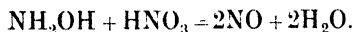
Hydroxylamine and its salts in solution act as *powerful reducing agents*. They precipitate red cuprous oxide from Fehling's solution (p. 726), purple metallic gold from gold chloride, and in *acid* solutions reduce ferric to ferrous salts. The hydroxylamine is oxidised to nitrous oxide :



In *alkaline* solution, hydroxylamine oxidises ferrous hydroxide to ferric hydroxide and is reduced to ammonia :



The salts on heating with nitric acid evolve nitric oxide :



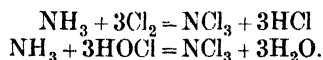
When mixed with a solution of a nitrite and acidified, they evolve nitrous oxide. Hyponitrous acid is formed as an intermediate product :



In absence of water hydroxylamine can act as a very feeble acid : with lime it gives $\text{HOCa}\cdot\text{O}\cdot\text{NH}_2$, and with calcium $(\text{H}_2\text{NO})_2\text{Ca}$, both explosive on heating. Fulminic acid, $\text{C}\cdot\text{N}\cdot\text{OH}$, on boiling with hydrochloric acid gives hydroxylamine. If a solution of a hydroxylamine salt is mixed with sodium nitroprusside solution and a little sodium hydroxide, a red colour appears on heating (test).

Nitrogen trichloride.—Dulong (1811) by the action of chlorine on a solution of ammonium chloride obtained a yellow oil which was violently

explosive. He lost an eye and three fingers in the research. Dulong did not publish his work: an abstract of it by Thenard and Berthollet appeared later. In the meantime Davy (1813) obtained the compound by the same method, and concluded that its formula was NCl_4 . Balard (1834) prepared it by the action of hypochlorous acid on ammonia, and Kolbe (1847) found that it separates at the anode in the electrolysis of ammonium chloride solution at 28° . The substance is nitrogen trichloride, NCl_3 :



Nitrogen trichloride may be prepared by inverting a flask of chlorine over a 25 per cent freshly-prepared solution of ammonium chloride, a lead saucer being placed under the mouth of the flask (Fig. 281).

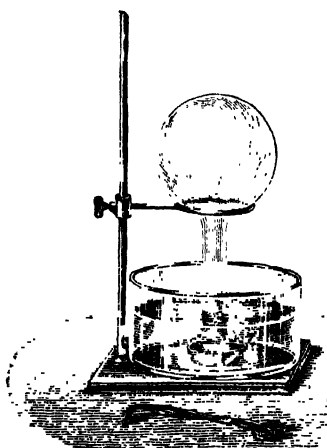


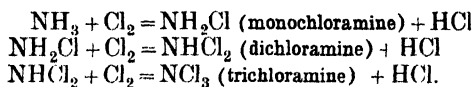
FIG. 281.—Preparation of nitrogen trichloride.

(According to Noyes, ammonium sulphate solution gives better results than ammonium chloride.) The chlorine is absorbed and only drops of nitrogen trichloride float on the surface of the solution. These fall into the lead saucer, which should be removed when a little liquid has collected in it. If a little turpentine is passed by a long pipette into the flask, covered with a strong box, a violent explosion results, the glass being completely shattered. The drop of oil in the dish also explodes violently when touched with a feather dipped in turpentine. *This experiment is dangerous and should not be made by a student.*

A solution of nitrogen trichloride in benzene is formed by acidifying a solution of bleaching powder with hydrochloric acid, adding ammonium chloride, and shaking with benzene.

Nitrogen trichloride vapour has an irritating smell and attacks the eyes: the sp. gr. of the liquid is 1.65, it freezes below -40° (Davy). The liquid explodes when heated to about 100° , by shock, in direct sunlight, and in contact with phosphorus, many oils (including turpentine), fused caustic potash, phosphine, rubber, and nitric oxide.

Gattermann (1888) found that the oil has the formula NCl_3 if the action of chlorine is prolonged, but the chlorination of ammonia proceeds in three stages:

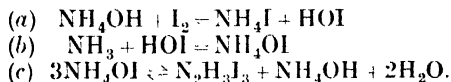


The analysis was carried out by decomposing with ammonia: $\text{NCl}_3 + 4\text{NH}_3 = \text{N}_2 + 3\text{NH}_4\text{Cl}$, and precipitating the chloride with silver

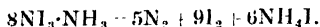
nitrate. The percentage of chlorine was found to be 89.1; NCl_3 requires 89.17.

Monochloramine NH_2Cl is formed as unstable colourless crystals, m. pt. -66° , when ammonia and sodium hypochlorite are mixed in solution in equimolecular proportions, the liquid is distilled in a vacuum, the vapour dried with K_2CO_3 and condensed in liquid air: $\text{NaOCl} \cdot \text{NH}_3 = \text{NaOH} + \text{NH}_2\text{Cl}$. **Dichloramine** NHCl_2 is obtained in solution (Chapin, 1929) by the action of chlorine on a solution of ammonium sulphate buffered to an acidity of pH 4.5 to 5, when it is the sole product, and also by the acidification of monochloramine solution. **Monobromamine** NH_2Br and **dibromamine** NHBr_2 , are formed by the action of ammonia gas on a solution of bromine in ether: $2\text{NH}_3 + \text{Br}_2 = \text{NH}_2\text{Br} + \text{NH}_4\text{Br}$, and $\text{NH}_2\text{Br} + \text{Br}_2 = \text{NHBr}_2 + \text{HBr}$. By the action of NCl_3 on KBr , Millon obtained a dark-red volatile explosive oil, possibly **nitrogen tribromide** NBr_3 . **Nitrogen trifluoride** NF_3 is a colourless rather inert gas, b. pt. -119° , obtained by the electrolysis of fused NH_4HF_2 ; when mixed with hydrogen and kindled it explodes violently, giving nitrogen and hydrogen fluoride (Ruff, 1928): $2\text{NF}_3 + 3\text{H}_2 = \text{N}_2 + 6\text{HF}$.

Nitrogen iodide.—By the action of iodine on ammonia solution (Courtois (1812) obtained a black explosive powder. This was examined by Gay-Lussac and by Davy (1814), who showed that it contained nitrogen and iodine. Gladstone (1851-54) gave it the formula NHI_2 , whilst Gay-Lussac, and Stahlschmidt (1863), considered it to be NI_3 . Bunsen (1852), by mixing alcoholic solutions of iodine and ammonia, obtained $\text{N}_2\text{I}_3\text{H}_3$, i.e. $\text{NI}_3 \cdot \text{NH}_3$. Szuhay (1893) by suspending "iodide of nitrogen" in water and adding ammoniacal silver nitrate solution, obtained a black explosive powder which he stated was NAgI_2 , and hence he supposed that nitrogen iodide is NHI_2 . Chattaway (1900) found, however, that the first product of the action of iodine on aqueous ammonia is a dark-red crystalline compound, $\text{NI}_3 \cdot \text{NH}_3$, and he confirmed the observation of Selivanoff (1894) that hypoiodous acid is the first product of the reaction, reacting with more ammonia to form iodide of nitrogen, possibly by decomposition of ammonium hypoiodite:



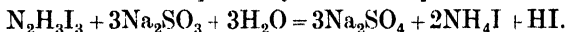
Triturate gently 1 gm. of iodine with concentrated ammonia. A black powder is formed, which is filtered off, and is fairly stable when moist. The filter-paper is torn into a number of pieces, which are allowed to dry spontaneously. If one portion is touched with a stick, it explodes—sometimes spontaneous explosion occurs. If two portions are close together and one is exploded, the shock brings about the explosion of the other portion. Violet fumes of iodine are evolved:



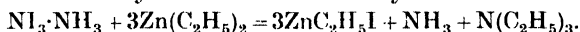
If a solution of iodine in KI is added drop by drop to a solution of ammonia, with shaking, the liquid at first remains clear and gives the reactions of hypoiodous acid (e.g. a brown precipitate with MnSO_4). On

further addition of iodine, a black precipitate of iodide of nitrogen is formed. If a large amount of concentrated ammonia is added this re-dissolves, showing that reaction (c) above is reversible.

Nitrogen iodide is decomposed by sodium sulphite :



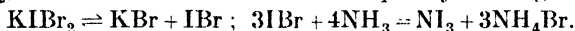
The free acid may be titrated with baryta and the iodide with silver nitrate, and so the composition determined. Silberrad (1905) confirmed the formula by the action of zinc ethyl on the substance :



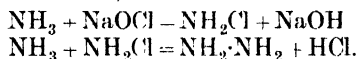
He showed that Szuhay's compound is $\text{NI}_3 \cdot \text{AgNH}_2$.

Nitrogen iodide is an active oxidising agent, oxidising sulphites to sulphates, arsenious acid to arsenic acid, etc. Each atom of iodine has an oxidising effect of an atom of oxygen, as in hypiodous acid HOI.

Nitrogen tri-iodide NI_3 is obtained by the action of gaseous ammonia on KIBr_2 , and remains as a black residue on quickly washing with water:



Hydrazine.—Hydrazine, N_2H_4 , prepared by Curtius in 1887 from organic compounds, was obtained by Raschig in 1907 by the action of sodium hypochlorite on ammonia solution in the presence of a little glue. Monochloramine, first formed, reacts with ammonia to form hydrazine :



To 200 ml. of 20 per cent ammonia add 5 ml. of 1 per cent solution of glue and 100 ml. of freshly made NaOCl solution (obtained by saturating cold 5 per cent NaOH solution with chlorine). Heat rapidly to boiling and keep at the boiling point for half an hour. Cool and acidify with dilute sulphuric acid. The hydrazine sulphate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ (6 gm.), crystallises out and is filtered in a Buchner funnel.

If hydrazine sulphate is distilled under reduced pressure with concentrated potassium hydroxide solution, with a condenser without rubber or cork connections, a colourless fuming liquid, b. pt. 119° or $47^\circ/26$ mm., is obtained. This is called *hydrazine hydrate*, but is a solution of maximum boiling point. The solution may be concentrated to 95 per cent by distilling it with xylene, which carries over the water. If the hydrate is distilled with its own weight of sodium hydroxide in small pieces, **anhydrous hydrazine** passes over at 150° as a liquid which solidifies on cooling in colourless crystals, m. pt. 1.4° , b. pt. 113.5° . Anhydrous hydrazine may also be prepared from the hydrochloride and sodium methoxide, in a similar way to hydroxylamine (p. 524). There is a solid hydrate $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, m.pt.— 51.7° .

Hydrazine and the hydrate readily absorb moisture and carbon dioxide from the air, are freely soluble in water and alcohol, and are poisonous. Anhydrous hydrazine decomposes on heating : $3\text{N}_2\text{H}_4 = \text{N}_2 + 4\text{NH}_3$. It inflames in dry oxygen, reacts readily with halogens : $2\text{I}_2 + \text{N}_2\text{H}_4 = 4\text{HI} + \text{N}_2$, and explodes in contact with potassium permanganate. By the action of sodium on anhydrous hydrazine in

absence of oxygen, crystalline solid $\text{H}_2\text{N}\cdot\text{NHNa}$ is obtained, which explodes violently in presence of oxygen or moisture.

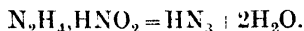
Hydrazine is a very weak base: when anhydrous it liberates ammonia from ammonium chloride. It forms two series of salts, *e.g.* the hydrochlorides $\text{N}_2\text{H}_4\cdot\text{HCl}$ and $\text{N}_2\text{H}_4\cdot 2\text{HCl}$; and the sulphates $2\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$. The ordinary hydrazine sulphate is $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, perhaps $\text{N}_2\text{H}_5\cdot\text{HSO}_4$. The salts are hydrolysed in solution. Double salts, *e.g.* $\text{ZnCl}_2\cdot\text{N}_2\text{H}_4\cdot 2\text{HCl}$, are known.

Hydrazine and its salts are powerful reducing agents, precipitating gold, silver and platinum from their salts, reducing alkaline copper solutions to cuprous oxide: $4\text{CuO} + \text{N}_2\text{H}_4 = 2\text{Cu}_2\text{O} + 2\text{H}_2\text{O} + \text{N}_2$; ferric salts to ferrous salts, and iodates to iodides: $3\text{N}_2\text{H}_4 + 2\text{H}_2\text{SO}_4 + 2\text{KIO}_3 = 2\text{HI} + 2\text{KHSO}_4 + 6\text{H}_2\text{O} + 3\text{N}_2$. The hydrazine is oxidised to nitrogen and water: $\text{N}_2\text{H}_4 + 2\text{O} = \text{N}_2 + 2\text{H}_2\text{O}$. Hydrazine may be determined by titration with iodine in presence of sodium bicarbonate: $\text{N}_2\text{H}_4 + 2\text{I}_2 = \text{N}_2 + 4\text{HI}$, or with potassium permanganate in presence of dilute sulphuric acid: $\text{N}_2\text{H}_4 + 2\text{O} = \text{N}_2 + 2\text{H}_2\text{O}$.

Hydrazoic acid.—Hydrazoic acid (or *azoimide*) HN_3 was obtained by Curtius in 1890 from organic compounds. It is formed by the careful oxidation of hydrazine with nitric acid or hydrogen peroxide: $3\text{N}_2\text{H}_4 + 5\text{O} = 2\text{HN}_3 + 5\text{H}_2\text{O}$.

Warm 1 gm. of hydrazine sulphate with 4 ml. of HNO_3 of sp. gr. 1.3 in a test-tube, and lead the vapours into a solution of silver nitrate. A white curdy precipitate of silver azide AgN_3 is formed. This is explosive when dry. It is soluble in ammonia (*cf.* Ag^+). Lead azide $\text{Pb}(\text{N}_3)_2$ is used as a detonator in place of mercury fulminate.

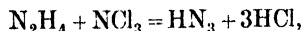
Hydrazoic acid is formed by the decomposition of hydrazine nitrite under special conditions (*cf.* $\text{NH}_3\cdot\text{HNO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$):



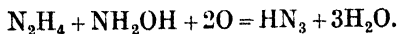
If hydrazine is added to ethyl or amyl nitrite and alkali, sodium azide is formed, and a precipitate of silver azide is produced when hydrazine is added to a saturated solution of silver nitrite. Sodium azide is formed by fusing sodamide with sodium nitrate:



Hydrazoic acid is formed by the action of hydrazine on a solution of nitrogen trichloride in benzene:



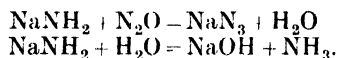
and by oxidising a mixture of hydrazine and hydroxylamine with chromic acid or hydrogen peroxide:



Active nitrogen forms azides with sodium, potassium, rubidium, and caesium; with sodium a nitride Na_3N is first formed.

Wislicenus (1892) first prepared hydrazoic acid from inorganic materials. Sodamide NaNH_2 is prepared by passing dry ammonia

over sodium in porcelain boats in a hard-glass tube heated at 150°–250°: $2\text{Na} + 2\text{NH}_3 = 2\text{NaNH}_2 + \text{H}_2$. The ammonia is then displaced by a current of dry nitrous oxide and the tube heated at 190°. The sodamide swells up and ammonia is evolved:

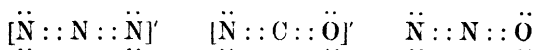


When no more ammonia is evolved the tube is cooled, and the pumice-like mass of NaN_3 and NaOH distilled with dilute sulphuric acid, when a solution of hydrazoic acid HN_3 comes over.

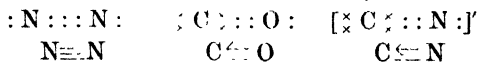
The solution is fractionated, and finally distilled with fused calcium chloride, when anhydrous hydrazoic acid is formed. This is a colourless mobile liquid, b. pt. 37°, m. pt. -80°, with a nauseous smell. It is dangerously poisonous and explosive. It dissolves readily in water, forming a corrosive acid liquid, in which about 1 per cent of the acid is ionised: $\text{HN}_3 \rightleftharpoons \text{H}^+ + \text{N}_3^-$. The solution readily dissolves iron, zinc, copper, etc., with formation of azides, ammonia, a trace of hydrazine, and evolution of nitrogen: $\text{Zn} + 3\text{HN}_3 = \text{Zn}(\text{N}_3)_2 + \text{N}_2 + \text{NH}_3$. With magnesium a little hydrogen is evolved. The reaction with nitrous acid is quantitative: $\text{HN}_3 + \text{HNO}_2 = \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$.

The azides give a blood-red colour with ferric chloride, resembling thiocyanate but discharged by hydrochloric acid; with silver nitrate they give a white curdy precipitate of silver azide AgN_3 , soluble in ammonia, and exploding at 250°. By neutralising the acid with ammonia and hydrazine, respectively, the salts NH_4N_3 (i.e. N_4H_4) and $\text{N}_2\text{H}_5\text{N}_3$ (i.e. N_5H_5) are obtained in colourless explosive crystals.

The vapour density of hydrazoic acid corresponds with HN_3 . The constitution was represented by Thiele as $\text{N} \equiv \ddot{\text{N}} - \text{NH}$. This may be written $\overset{\times \times}{\underset{\times \times}{\text{N}}} \vdots \text{N} \vdots \ddot{\text{N}} \vdots \text{H}$ or $\text{N} \equiv \ddot{\text{N}} - \text{NH}$. The formulae of the azide ion, the cyanate ion, and the neutral nitrous oxide molecule are similar:



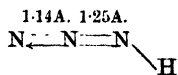
The linear structure of the azide ion in crystals is proved by X-ray analysis. The electronic formulae of the nitrogen and carbon monoxide molecules, and of the cyanide ion, are also very similar:



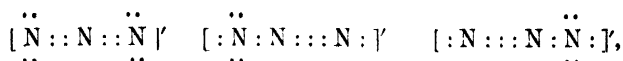
Chlorazide N_3Cl is a colourless very explosive gas obtained by the action of sodium hypochlorite solution and boric acid on sodium azide. **Iodazide** N_3I is a pale-yellow explosive solid obtained by the action of iodine on silver azide.

Cyanogen azide $(\text{CN} \cdot \text{N}_3)_2$, **sulphuryl azide** $\text{N}_3 \cdot \text{SO}_2 \cdot \text{N}_3$, and **azido-dithiocarbonyl acid** $\text{N}_3 \cdot \text{CS} \cdot \text{SH}$, are also known.

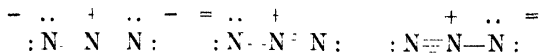
The hydrazoic acid molecule has a hydrogen atom linked by a bond at an angle to the linear azide group:



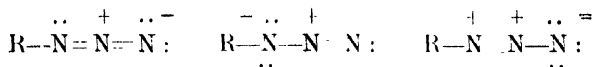
and the esters have a similar structure with the group R taking the place of H. The azide ion is a resonance hybrid of three forms :



or with the alternative formulation of the co-ordinate link (p. 413) :



All are equally important, so that the two bonds are of the same length, 1.15A. In these formulae the ionic charge is also shown. Of the three corresponding structures of a covalent azide (*e.g.* an ester) :



the third disagrees with the adjacent charge rule (p. 438) and only the first two are involved, the *azide group* ---N_3 now being unsymmetrical.

CHAPTER XXX

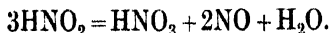
OXIDES AND OXY-ACIDS OF NITROGEN

Oxides and oxy-acids of nitrogen.—The following table of oxides and oxy-acids of nitrogen may be compared with that of the oxy-compounds of chlorine (p. 262) :

Nitrous oxide N_2O	→	{ Hyponitrous acid $HO\cdot N:N\cdot OH$ Nitramide $NO_2\cdot NH_2$
Nitric oxide NO	→	Hyponitric acid $HON:NO_2H$
Dinitrogen trioxide N_2O_3	→	↗ Nitrous acid HNO_2
Nitrogen dioxide (or dinitrogen tetroxide) NO_2 or N_2O_4	→	↘ Nitric acid HNO_3
Dinitrogen pentoxide N_2O_5	→	

A full arrow shows that the oxide is a true acid anhydride, forming the corresponding acid by reaction with water; a dotted arrow indicates a formal relation only. In addition to the compounds shown in the table, the following have been described: **hydronitrous acid** H_2NO_2 ($\cdot NO + H_2O$) known as the sodium salt Na_2NO_2 ; a higher oxide of nitrogen which is probably **dinitrogen hexoxide** N_2O_6 , and a higher oxyacid, either **pernitric acid** HNO_4 ($N_2O_6 + H_2O = HNO_4 + HNO_3$) or **pernitrous acid** $HNO_2\cdot O$ (isomeric with nitric acid).

The union of nitrogen and oxygen.—Nitrogen and oxygen combine directly at high temperatures to form colourless **nitric oxide**: $N_2 + O_2 \rightleftharpoons 2NO$. With excess of oxygen this on cooling forms red **nitrogen dioxide**: $2NO + O_2 \rightleftharpoons 2NO_2$. Nitrogen dioxide dissolves in water to form a solution of **nitrous** and **nitric acids**: $2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3$. Nitrous acid is unstable, the solution becoming pale blue owing to the formation of **nitrous anhydride** N_2O_3 : $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$. This also decomposes, forming gaseous nitrogen dioxide and nitric oxide: $N_2O_3 \rightleftharpoons NO_2 + NO$. Some nitrous acid also decomposes into nitric acid and nitric oxide:



The nitric oxide is again oxidised if excess of oxygen is present, and finally all the oxides of nitrogen are converted into dilute nitric acid.

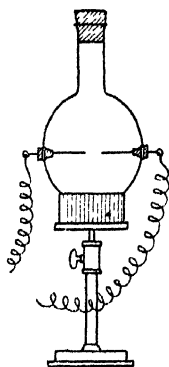


FIG. 282.—Combination of nitrogen and oxygen by sparking.

Pass a series of sparks through dry air in a globe (Fig. 282). After a time this becomes yellowish in colour, and if shaken with litmus solution the latter is turned red.

Nitric acid is also formed when a hydrogen flame burns in oxygen containing a little nitrogen, and when a mixture of detonating gas (2 vols. of $H_2 + 1$ vol. of O_2) with air is exploded by a spark. If the volume of air is more than double that of the detonating gas, the temperature of explosion is too low to form nitric acid: no acid is formed on exploding a mixture of hydrogen and air, as was shown by Cavendish (1781).

Cavendish (1785) passed sparks through a mixture of air and oxygen confined over mercury and potassium hydroxide solution in an inverted V-tube (Fig. 283). The oxides of nitrogen were absorbed by the alkali and the residual oxygen was then absorbed by a solution of liver of sulphur (potassium sulphide), only a very small bubble of gas remaining (probably argon; see p. 962).

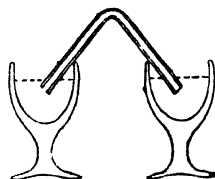


FIG. 283.—Cavendish's apparatus for sparking air over potash solution.

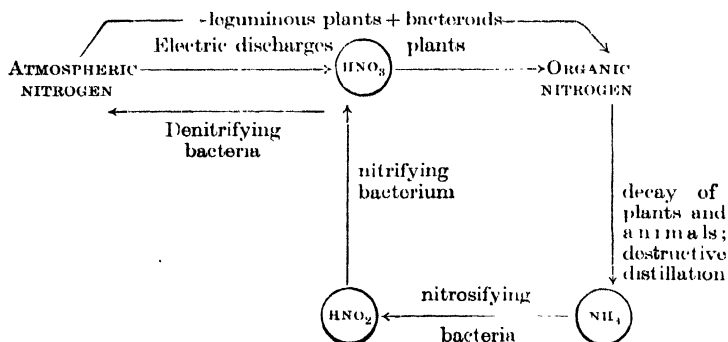
Cavendish says: "We may safely conclude that in the present experiments the phlogisticated air [N] was enabled, by means of the electric spark, to unite to, or form a chemical combination with, the dephlogisticated air [O], and was thereby reduced to nitrous [nitric] acid, which united with the soap-lees [potash] and formed a solution of nitre; for in these experiments those two airs actually disappeared, and nitrous acid was actually formed in their room."

The nitrogen cycle.—Nitric acid is formed by electrical discharges in the atmosphere, and is washed down by rain. It is estimated that 250,000 tons are produced in twenty-four hours. Leguminous plants can convert atmospheric nitrogen into organic nitrogen by the agency of micro-organisms (*Pseudomonas radicumicola*) which occur in nodules on the root. Algae, fungi, and mosses assimilate free nitrogen, and a bacterium, *Azotobacter chroococcum*, present in soil, fixes elementary nitrogen in presence of calcium carbonate. The organic nitrogen compounds elaborated by plants serve as food for herbivorous animals, and the proteins of the latter are utilised by carnivora.

When animals and plants die and decay, ammonia is formed. In the soil this is oxidised by *nitrosifying bacteria* to nitrites, and these by the *nitrifying bacterium* to nitrates, the latter again serving for the nourishment of plants. Part of the nitrogen is again set free by the action of *denitrifying bacteria* in the soil.

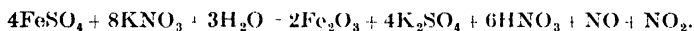
Pseudomonas radicumicola has one general species but it has to some extent become specialised by association with particular plants. It exists in the soil as minute rods in rapid motion, but when it enters the plant by way of the root-hairs it develops into larger rods which, when nodules are formed on the roots, associate into characteristic Y-shaped organisms called *bacteroids*. The *Azotobacter chroococcum*, a fairly large oval organism, plays a large part in forming and maintaining the stock of combined nitrogen in the soil. Both nitrosifying bacteria and the nitrifying bacterium obtain their carbon from carbon dioxide.

THE NITROGEN CYCLE



NITRIC ACID

Nitric acid seems to have been known in Europe about 1100 A.D., if not earlier. It was called *aqua fortis* and made by distilling nitre with green vitriol (ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$):



Glauber, about 1658, obtained concentrated fuming nitric acid by distilling nitre with oil of vitriol (sulphuric acid). It was known as *spiritus nitri Glauberi*. The presence of oxygen in nitric acid was demonstrated by Lavoisier in 1776 by heating nitrate of mercury, which evolved oxygen and nitric oxide. Scheele (1777) showed that the vapour is decomposed by heat and light. Cavendish (1785) proved that nitric acid contains nitrogen and oxygen (p. 533).

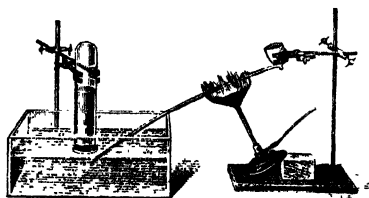


FIG. 284.—Decomposition of nitric acid by heat.

Arrange a clay tobacco pipe as shown in Fig. 284. Heat one part of the stem strongly with a bunsen burner, and pour 5 ml. of concentrated nitric acid into the bowl. The acid is decomposed on passing through the hot tube, and bubbles of oxygen collect in the test-tube.

Nitric acid is prepared in the laboratory by distilling potassium or sodium nitrate with concentrated sulphuric acid: $\text{KNO}_3 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{HNO}_3$. If excess of nitre is used at a high temperature, further decomposition occurs, the potassium (or sodium) hydrogen sulphate being converted into normal sulphate: $\text{KHSO}_4 + \text{KNO}_3 = \text{K}_2\text{SO}_4 + \text{HNO}_3$. A glass retort then usually cracks, and part of the nitric acid is decomposed: $4\text{HNO}_3 = 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2$. The oxides of nitrogen formed dissolve in the acid, colouring it yellow.

Add 49 gm. (26 ml.) of concentrated sulphuric acid to 50 gm. of powdered potassium nitrate in a stoppered retort and stir with a glass rod. Heat on

wire gauze and collect the nitric acid in a cooled receiver (Fig. 285). Notice the red gas at the beginning and end of the process. The acid obtained is yellow. Add a piece of copper foil to it; the metal does not usually dissolve. Add a few drops of water: the copper dissolves and red oxides of nitrogen are evolved (Andrews, 1837).

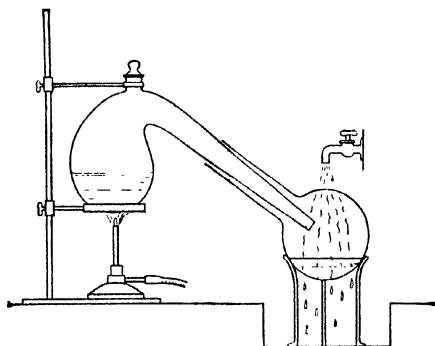


FIG. 285.—Preparation of nitric acid.

Nitric acid may be concentrated by distillation with concentrated sulphuric acid. Pure nitric acid is obtained by redistilling on a water-bath under reduced pressure and passing ozonised oxygen through the distillate, or by freezing 98 per cent acid, when colourless crystals, m. pt. -41.3° , separate. It is a colourless liquid of sp. gr. 1.52. The liquid and the vapour are slightly dissociated at the ordinary temperature: $2\text{HNO}_3 \rightleftharpoons \text{N}_2\text{O}_5 + \text{H}_2\text{O}$; the dissociation increases with the temperature and liquid anhydrous HNO_3 does not exist. A current of dry air passed through the liquid removes the more volatile N_2O_5 and an acid containing 98.62 per cent of HNO_3 remains.

Nitric acid begins to boil at 78.2° , with decomposition. When three-fourths have distilled, the residue contains 95.8 per cent of HNO_3 ; with further distillation an acid of maximum boiling point (120.5°) containing 68 per cent of HNO_3 is formed. This is also formed when weaker solutions are distilled. This acid corresponds approximately with $2\text{HNO}_3, 3\text{H}_2\text{O}$ but is not a definite hydrate; Roscoe showed that (as in the case of hydrochloric acid) the composition of the distillate is a function of the pressure. Two solid hydrates, $\text{HNO}_3, \text{H}_2\text{O}$ (m. pt. -38°) and $\text{HNO}_3, 3\text{H}_2\text{O}$ (m. pt. -18.5°) are known.

Nitric acid vapour is decomposed by light on exposure of a half-filled bottle; the nitrogen dioxide formed dissolves in the liquid and makes it yellow: $4\text{HNO}_3 = 4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O}$. The liquid in a completely filled bottle remains colourless. The yellow acid may be decolorised by warming to 60° – 80° , and bubbling dry air through it.

A yellow *fuming nitric acid*, containing oxides of nitrogen and used as an oxidising agent, is prepared by distilling nitre and sulphuric acid with a little starch, which reduces some nitric acid to N_2O_3 and N_2O_4 .

Heat is evolved and contraction occurs when concentrated nitric acid and water are mixed. The maximum effect occurs with the mixture $3\text{HNO}_3 + \text{H}_2\text{O}$, but no definite hydrate of this composition has been isolated.

The densities at 15° of mixtures of nitric acid and water are given in the table below.

Density	Per cent. HNO_3	Density	Per cent. HNO_3	Density	Per cent. HNO_3
1.050	8.99	1.250	39.82	1.450	77.28
1.100	17.11	1.300	47.49	1.500	94.09
1.150	24.84	1.350	55.79	1.510	98.10
1.200	32.36	1.400	65.30	1.520	99.67

Chemical properties of nitric acid.—Nitric acid is a strong acid, largely ionised in solution: $\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$. It is monobasic and forms salts, the nitrates, which are obtained by the action of nitric acid on the metals (when oxides of nitrogen, not hydrogen, are usually evolved), on the oxides or hydroxides, or on the carbonates. Acid nitrates, e.g. NH_4NO_3 , HNO_3 and $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$, are known.

Alkali nitrates on heating form nitrites and oxygen: $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$; ammonium nitrate gives nitrous oxide: $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$; nitrates of heavy metals form oxides, nitrogen dioxide and oxygen: $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$. Most nitrates are soluble in water; some basic nitrates (e.g. of lead and bismuth) are insoluble.

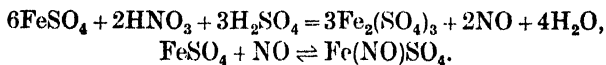
Nitric acid also acts as an oxidising agent. Hot concentrated nitric acid oxidises iodine to iodic acid HIO_3 . Phosphorus is oxidised to phosphorous and phosphoric acids (white phosphorus may cause an explosion), sulphur is oxidised to sulphuric acid, arsenious oxide to arsenic acid. Tin is oxidised by concentrated nitric acid in the cold with formation of red fumes and white hydrated stannic oxide. Burning charcoal burns brilliantly in concentrated nitric acid, and heated sawdust is inflamed by it.

Heat a little sawdust on a sand-bath until it begins to char, and pour over it a few drops of fuming nitric acid from a test tube. The sawdust burns.

Oil of turpentine explodes with concentrated nitric acid, with evolution of black clouds of carbon. Alcohol is violently oxidised, with the production of a variety of substances, and sometimes with explosion.

Hydrogen sulphide is not oxidised by pure nitric acid, but in presence of nitrogen oxides it is decomposed with separation of sulphur (see p. 457). Stannous chloride in hydrochloric acid is oxidised to stannic chloride and the nitric acid is reduced to hydroxylamine and ammonia.

Ferrous salts reduce nitric acid to nitric oxide NO , which in the cold dissolves in the excess of ferrous salt to form a black solution, from which nitric oxide is evolved on heating:



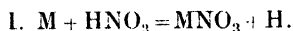
This is used in the "ring test" for nitric acid and nitrates. In the case of nitrates, *concentrated* sulphuric acid must be added before the colour appears (*nitrites* give the reaction with *dilute* acid).

Dissolve a few crystals of ferrous sulphate in a cold dilute solution of potassium nitrate in a test-tube, and pour concentrated sulphuric acid carefully into the liquid so as to form a heavy layer below. At the junction of the liquids a black ring (purple if only traces of nitrate are present) is formed. On shaking, the black colour disappears and bubbles of nitric oxide are evolved.

Other tests for nitric acid and nitrates are : (i) the red colour produced with a solution of brucine in concentrated sulphuric acid ; (ii) the deep-blue colour with a solution of diphenylamine in concentrated sulphuric acid ; (iii) the evolution of red oxides of nitrogen when the substance is heated with concentrated sulphuric acid and copper turnings ; (iv) *nitron* reagent (1 per cent in 5 per cent acetic acid) forms a white crystalline precipitate of nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$, on adding 5 drops of reagent and 1 drop of dilute sulphuric acid to 5 ml. of nitrate solution.

The action of nitric acid on metals.—Nearly all metals, except platinum, rhodium, iridium, tantalum, and gold, are attacked by dilute or concentrated nitric acid. Tin, arsenic, antimony, tungsten and molybdenum are converted into oxides. The remaining metals form nitrates. Aluminium is scarcely attacked by cold nitric acid ; iron and chromium become "passive" in the concentrated acid, and lead is covered with a protective film of nitrate. During the reactions, part of the acid is reduced to the oxides NO_2 , NO , and N_2O , free nitrogen, hydroxylamine, and ammonia. The products depend on the metal, temperature, concentration of the acid, and the presence of the products of reaction. Hydrogen is evolved only by magnesium or manganese acting on cold 1 or 2 per cent nitric acid : $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$.

H. E. Armstrong and Acworth (1877) suggested that the *primary reaction* in *all* cases is the liberation of nascent hydrogen :



This nascent hydrogen reduces the nitric acid and further reactions occur :

II. *Secondary reactions*, probably in definite stages :

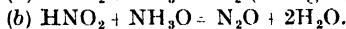
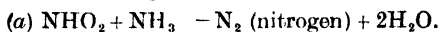
- (a) $HNO_3 + 2H = HNO_2$ (nitrous acid) + H_2O .
- (b) $2HNO_3 + 8H = H_2N_2O_2$ (hyponitrous acid) + $4H_2O$.
- (c) $HNO_3 + 6H = NH_3O$ (hydroxylamine) + $2H_2O$.
- (d) $HNO_3 + 8H = NH_3$ (ammonia) + $3H_2O$.

III. *Tertiary reactions*, in which the secondary products interact :

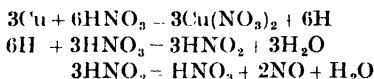
(1) *decomposition* into simpler compounds :

- (a) $3HNO_2 = HNO_3 + 2NO$ (nitric oxide) + H_2O .
- (b) $2HNO_2 = N_2O_3$ (nitrous anhydride) + H_2O .
- (c) $H_2N_2O_2 = N_2O$ (nitrous oxide) + H_2O .

(2) *double decomposition* :



The action on *copper* would be represented as follows :



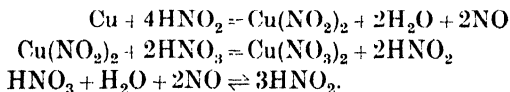
∴ by addition $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$.

According to Divers some metals give nitric oxide but no hydroxylamine or ammonia : *e.g.* Ag, Cu, Bi, Hg ; other metals give NH_3 , or NH_3O , and N_2O : *e.g.* Fe, Zn, Sn, Cd, Mn, Mg (Mn and Mg also give H_2). The product depends on the concentration and temperature of the acid (concentrated nitric acid gives mainly nitrogen dioxide with copper : $\text{Cu} + 4\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$), and also on the accumulation of the salt in the solution, since the prolonged action of dilute nitric acid on copper gives nitrogen and nitrous oxide.

Millon (1842) and Veley (1890) showed that *pure* nitric acid in the absence of nitrous acid scarcely acts on copper, silver, bismuth or mercury. Other metals react in the absence of nitrous acid, but more slowly than when it is present. Since nitrous acid is formed in the reaction, the velocity of the reaction increases as it proceeds.

Take three pieces of clean copper foil and immerse them in three glasses containing : (a) 50 ml. of 50 per cent nitric acid ; (b) 50 ml. of this nitric acid + 5 ml. of hydrogen peroxide (20 vols.) ; (c) 50 ml. of nitric acid + 1 ml. of hydrazine hydrate solution. The foil in (a) is at once violently attacked ; those in (b) and (c) remain for a time without change. The hydrogen peroxide oxidises nitrous acid : $\text{HNO}_2 + \text{H}_2\text{O}_2 = \text{HNO}_3 + \text{H}_2\text{O}$; whilst hydrazine decomposes it.

According to Millon and Veley nitric oxide is a primary product, formed from traces of nitrous acid : a green solution of copper nitrite is formed which is then decomposed by nitric acid to reproduce nitrous acid :



The nitric oxide reduces nitric acid to nitrous acid, and nitric oxide is evolved only at a certain concentration of nitrous acid.

The manufacture of nitric acid.—Nitric acid is made on the large scale by distilling sodium nitrate with concentrated sulphuric acid in an iron retort :



One or two tons of previously dried sodium nitrate (Chile nitre) are heated with rather more than this weight of concentrated sulphuric acid (93 per cent H_2SO_4) in a large cast-iron pot, built in a brickwork furnace so as to

allow of very uniform heating (Fig. 286). Nitric acid vapour does not attack iron, which is corroded by the liquid acid. At the top of the retort is a manhole for introducing the charge, and an outlet for the acid vapour.

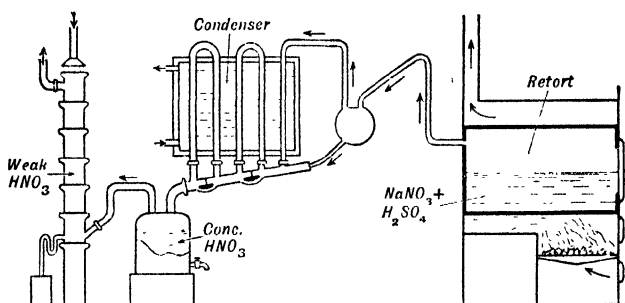
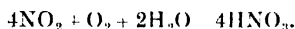


FIG. 286.—Manufacture of nitric acid by distilling sodium nitrate with concentrated sulphuric acid.

The acid is condensed in some type of cooler, consisting of vitreous silica spirals cooled in water, stoneware U-tubes or horizontal glass tubes cooled partly by air and water, S-shaped tubes of silicon iron, or large stoneware Woulfe's bottles. The red oxides of nitrogen also produced are condensed by water in a stoneware tower at the end, packed with hollow stoneware cylinders or balls :



In the *Valentiner process* (1891) the apparatus is air-tight, and a vacuum is maintained by an air-pump. The distillation under reduced pressure (25 cm.) takes place at a lower temperature (100° – 150°), so that there is less decomposition, and the reaction also occurs more rapidly than in the ordinary process.

The liquid residue in the retort is run out and allowed to solidify ; it is a mixture or compound of about equimolecular proportions of NaHSO_4 and Na_2SO_4 , and is called *nitre cake*.

The arc process.—The union of atmospheric nitrogen and oxygen at the high temperature of the electric arc was demonstrated by Crookes in 1892 ; a small experimental plant was worked in Manchester in 1899. As carried out from 1902 in Norway at Notodden and Rjukan, the *Birkeland and Eyde process* utilised 350,000 horse-power derived from water-power, but it is now replaced by ammonia synthesis and oxidation of ammonia.

Air is drawn through the flat circular furnace (Fig. 287), in which an alternating-current electric arc burning between water-cooled copper poles is spread out by an electromagnet into an

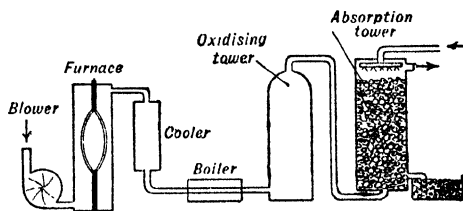
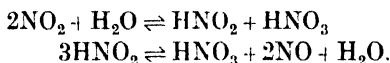


FIG. 287.—Diagram of the arc process for producing nitric acid from the atmosphere.

apparent disc, the temperature of which is about 3000°. In this flame combination of oxygen and nitrogen occurs: $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$. At 3000° the equilibrium yield of NO is 5 per cent by volume; at 1500° it is only 0.4 per cent. Since the reaction absorbs heat, the yield is greater at higher temperatures (p. 294). The gas after rapid cooling to "freeze" the equilibrium leaves the furnace at 1000°, containing 1 per cent of NO, passes through iron pipes lined with brick to the firebox of a tubular boiler, where it is cooled to 150° with production of steam which is used to evaporate solutions formed in the process, and then passes through large aluminium pipes exposed to the air where it cools to 50°.

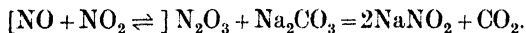
When the gas has cooled below 600°, formation of nitrogen dioxide begins: $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$; this is somewhat slow, since it is a termolecular reaction, and to give time the gas passes through a large empty iron oxidising tower, and then to the three or four gigantic absorption towers, 65–80 ft. high and 18 ft. diameter, built of granite slabs and packed with broken quartz over which water is circulated. In these towers nitric acid is formed:



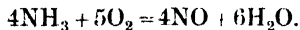
The NO is reoxidised by the excess of air present, forming NO_2 , which re-enters the reaction. Nearly all the nitrous acid is so removed from the solution, and 30 per cent nitric acid runs from the first tower, the acid having been pumped from the final tower through all the towers in succession.

The dilute nitric acid is neutralised with limestone to form calcium nitrate, which is evaporated and exported as a fertiliser ("Norge salpeter"), or is concentrated by distilling it with concentrated sulphuric acid under reduced pressure.

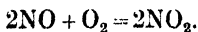
When the gases become very dilute, oxidation of NO is very slow, and a mixture of NO and NO_2 passes from the last absorption tower (about 85 per cent of the oxides of nitrogen having by this time been absorbed) into an iron tower packed with quartz, down which a solution of sodium carbonate trickles. This absorbs nearly all the residual oxides of nitrogen to form chiefly sodium nitrite with some nitrate:



The oxidation of ammonia.—In 1788, the Rev. Isaac Milner, President of Queens' College, Cambridge, found that ammonia gas passed over heated manganese dioxide is oxidised to nitric oxide, which can be oxidised with air to nitrogen dioxide, and this reacts with water to form nitric acid. The French chemist Kuhlmann in 1839 found that ammonia is oxidised to nitric oxide by passing a mixture of ammonia gas and air over heated platinum, acting as a catalyst:



The colourless gas on cooling becomes red, from oxidation of the nitric oxide to nitrogen dioxide:

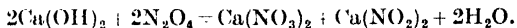


Pass a current of air through ammonia solution in a wash-bottle, and lead the mixed gas over a small roll of platinum foil heated to dull redness in a hard-glass tube. Notice the formation of red gas and white fumes in a globe attached to the tube.

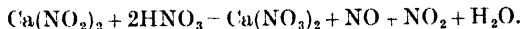
The best results are obtained when the gas passes very rapidly over the catalyst; with a slow current of gas much free nitrogen is produced: $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$. An excess of oxygen above that required to form nitric oxide is necessary. A mixture of 1 vol. of purified ammonia gas and 7.5 vols. of air filtered from dust is preheated to about 500° by utilising the heat of reaction in a counter-current apparatus (*cf.* p. 472), and is passed through a converter (*Fig.* 288) containing two fine platinum gauzes in contact, when the exothermic reaction proceeds automatically. More than 90 per cent of the ammonia is oxidised to nitric oxide, and 1 sq. ft. of double catalyst will produce 1.7 tons of nitric acid in 24 hours. The rate of conversion is much greater with a mixture of ammonia and oxygen, $\text{NH}_3 + 2\text{O}_2$, with sufficient steam to render it non-explosive, and nitric acid may then be obtained directly by cooling the gas from the converter.

The exit gas from the converter when air is used, containing NO, nitrogen, some oxygen, and steam, is cooled and passed into packed stainless steel towers through which water circulates. Formation of nitric acid occurs as in the arc process (p. 540). The cooled gas may also be compressed by pumps into stainless steel tanks containing water. Modern processes aim at converting ammonia and oxygen (obtained as by-product in ammonia synthesis) into nitric acid.

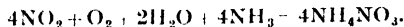
If the cooled oxidised gas is passed into milk of lime, calcium nitrite and nitrate are formed:



When all the lime is neutralised, nitric acid is formed in the solution by reactions previously explained. This decomposes the nitrite into nitrate and oxides of nitrogen, which are fully oxidised to NO_2 by air and passed into another absorber of milk of lime:



If ammonia gas mixed with air is blown into the cooled and fully oxidised gas from the ammonia oxidation apparatus, solid ammonium nitrate is deposited as a powder:



Dinitrogen pentoxide.—The anhydride of nitric acid, dinitrogen pentoxide N_2O_5 , was obtained by Deville (1849) by the action of dry chlorine on gently heated silver nitrate:

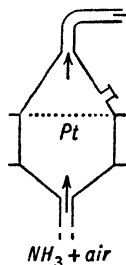
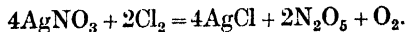
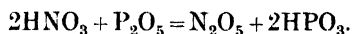


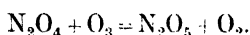
FIG. 288.—Ammonia oxidation converter.

It is best prepared by dehydrating concentrated nitric acid by phosphorus pentoxide (Weber, 1872) :

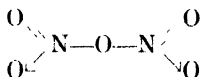


Pure concentrated nitric acid, freshly distilled over concentrated sulphuric acid, is put into a stoppered retort cooled in a freezing mixture, and pure phosphorus pentoxide added in slight excess in small quantities at a time. The mixture is distilled at as low a temperature as possible in a current of ozonised oxygen. The gas is passed through a phosphorus pentoxide tube, and then through a tube cooled in solid carbon dioxide and ether, when crystals of pure N_2O_5 are obtained.

Dinitrogen pentoxide is formed by passing ozonised oxygen into cooled liquid dinitrogen tetroxide :

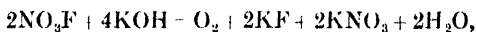


Dinitrogen pentoxide forms white very hygroscopic crystals, stable below 0° but decomposing slowly and becoming yellow at the ordinary temperature, even in sealed tubes : $2\text{N}_2\text{O}_5 = 2\text{N}_2\text{O}_4 + \text{O}_2$. They sublime on warming, and if not quite pure melt with decomposition at 29.5° to a dark-brown liquid, which decomposes into red NO_2 and oxygen at 50° . If suddenly heated, the crystals explode : they dissolve with a hissing noise in water, forming nitric acid : $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$. Phosphorus and potassium burn in the liquid pentoxide if slightly warmed: charcoal does not decompose it even on boiling, but burns brilliantly if previously kindled. Sulphur forms white vapours, condensing to crystals of nitrosyl disulphate $\text{S}_2\text{N}_2\text{O}_9$ (p. 558). A crystalline compound, $\text{N}_2\text{O}_5 \cdot 2\text{HNO}_3$, m. pt. 5° , is formed on cooling a solution of N_2O_5 in concentrated nitric acid. The structural formula of dinitrogen pentoxide is

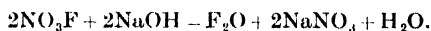


but owing to resonance the bonds become equivalent.

Halides of nitric acid.—The OH in nitric acid NO_2OH may be replaced by halogens or the ClO_4 radical. **Nitryl fluoride** NO_2F is a colourless very reactive gas, b. pt. -72.4° , m. pt. -166° , formed by the action of nitric oxide on excess of fluorine at the temperature of liquid oxygen : $4\text{NO} + \text{F}_2 = 2\text{NO}_2\text{F} + \text{N}_2$. **Nitryl chloride** NO_2Cl is a colourless gas, b. pt. -15° , m. pt. -145° , formed by the action of ozone on nitrosyl chloride : $\text{NOCl} + \text{O}_3 = \text{NO}_2\text{Cl} + \text{O}_2$, and in small amounts in other reactions, e.g. $4\text{NO}_2 + 3\text{HCl} = \text{NO}_2\text{Cl} + 2\text{NOCl} + \text{HNO}_3 + \text{H}_2\text{O}$. It is stable at 100° but decomposes at higher temperatures. **Fluorine nitrate** NO_3F is a colourless explosive gas, b. pt. -42° , formed by the action of fluorine on concentrated nitric acid or solid potassium nitrate. It is a powerful oxidising agent : $\text{NO}_3\text{F} + 2\text{KI} = \text{KNO}_3 + \text{KF} + \text{I}_2$. With concentrated alkali it evolves oxygen :



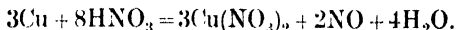
but with dilute alkali it forms fluorine monoxide :



Fluorine perchlorate FClO_4 is a colourless explosive gas formed from fluorine and perchloric acid, and is similar to fluorine nitrate. **Nitryl perchlorate** $\text{NO}_2(\text{ClO}_4)$ is a white crystalline solid, decomposing rapidly at 120° , formed from concentrated nitric and perchloric acids :



Nitric oxide.—Although nitric oxide appears to have been obtained by Van Helmont, Mayow, Hales, and Cavendish, it was first recognised as a distinct gas by Priestley (1772), who prepared it by the action of copper or mercury on dilute nitric acid and called it *nitrous air* :



Copper turnings are placed in a flask (Fig. 289) and a mixture of equal volumes of concentrated nitric acid and water are poured on them through

a thistle-funnel. At first, the air in the flask becomes red, due to the action of the nitric oxide on atmospheric oxygen : $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. The gas then becomes nearly colourless, but always has a slight yellowish tinge, due to a little NO_2 . This is removed when the gas is passed through water, and the jars fill with a colourless gas. The gas, especially in the later stages of the reaction, contains variable amounts of nitrogen and nitrous oxide. It may be purified by passing into a cold saturated solution of ferrous sulphate. A nearly black liquid is formed containing $\text{Fe}[\text{NO}]\text{SO}_4$, which on gentle heating evolves *nearly* pure nitric oxide. The gas so purified still contains 1/500 of its volume not absorbed by fresh ferrous sulphate solution, probably nitrous oxide.

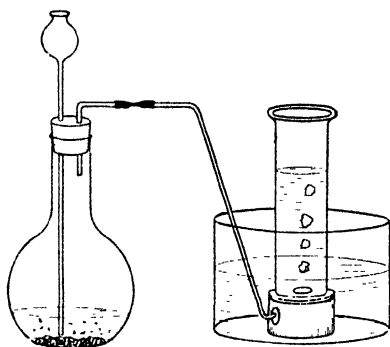
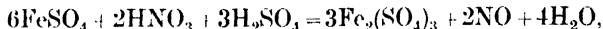
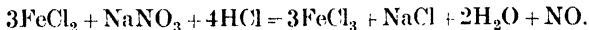


FIG. 289. —Preparation of nitric oxide from copper and nitric acid.

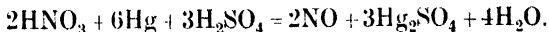
Nearly pure nitric oxide may be obtained by heating a mixture of potassium nitrate, ferrous sulphate, and dilute sulphuric acid :



or a solution of ferrous chloride in hydrochloric acid with sodium nitrate :



Very pure nitric oxide is obtained (W. Crum, 1847) by shaking mercury with concentrated sulphuric acid to which nitric acid or a nitrate has been added, and passing the gas over solid potassium hydroxide to remove any nitrogen dioxide :



This reaction is used in the estimation of nitrites or nitrates, or of oxides of nitrogen in commercial sulphuric acid. The solid substance is dissolved

in the least amount of water and passed into the Lunge nitrometer (Fig. 290), which consists of a graduated tube *A*, with a stopcock *B* communicating with a small cup *C*, and an outlet tube *D*, the whole being filled with mercury and provided with a levelling tube *E*. Concentrated sulphuric acid is then introduced and the mixture shaken violently with the mercury. The volume of nitric oxide is read off.

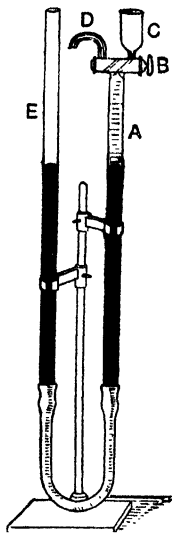
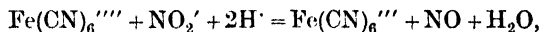
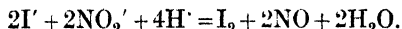


Fig. 290.—Lunge's nitrometer.

Pure nitric oxide is evolved on dropping a solution of sodium nitrite and potassium ferrocyanide into dilute acetic acid :



and by the action of sodium nitrite solution on an acidified solution of potassium iodide :



The pure gas should be collected over mercury, as it acts slightly on water, evolving traces of nitrous oxide : $4\text{NO} + \text{H}_2\text{O} = \text{N}_2\text{O} + 2\text{HNO}_2$.

Properties of nitric oxide.—Nitric oxide is a colourless gas, slightly heavier than air (normal density 1.3402 gm./lit.), and sparingly soluble in water. The volumes at S.T.P. absorbed by 1 vol. of water are :

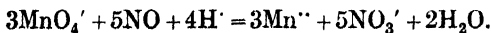
Temp. -	0°	15°	30°	60°
Vols. of NO	0.074	0.051	0.040	0.0295

It is not easily liquefied : the liquid, which has a somewhat darker blue colour than liquid oxygen, boils at -151.7° (when its density is 1.269), and freezes at -163.6° to a solid of the same colour. The critical temperature is -96° , and the critical pressure 64 atm.

Nitric oxide is freely soluble in cold ferrous sulphate solution, forming a black liquid, as was observed by Priestley. The maximum absorption corresponds with $\text{FeSO}_4(\text{NO})$, but the reaction is reversible, the absorption depending on the temperature, the concentration of the ferrous salt (other ferrous salts, e.g. FeCl_2 , also absorb NO), the pressure, and the presence of other salts : $\text{FeSO}_4 + \text{NO} \rightleftharpoons \text{FeSO}_4(\text{NO})$. The gas is readily evolved on heating. Manchot regards the compound as a nitroso-compound $[\text{Fe}(\text{NO})]\text{SO}_4 \rightleftharpoons \text{FeNO}^+ + \text{SO}_4^{2-}$, the nitric oxide being in the cation. Cobalt, nickel, manganese, chromium, and cuprous chlorides also absorb nitric oxide. The compound $\text{Fe}(\text{NO})\text{SeO}_4$ is known in the solid state.

Liquid or compressed nitric oxide slowly decomposes into N_2O_3 and nitrous oxide, N_2O : $4\text{NO} = \text{N}_2\text{O}_3 + \text{N}_2\text{O}$. This reaction also occurs slowly in presence of water (see above) or alkali : $4\text{NO} + 2\text{NaOH} = \text{N}_2\text{O} + 2\text{NaNO}_2 + \text{H}_2\text{O}$.

Nitric oxide is slowly absorbed by acidified potassium permanganate solution :

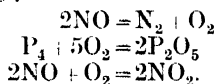


It is not appreciably absorbed by alkali, but dissolves in alkaline sulphite solution, forming a dinitrososulphite, $\text{Na}_2(\text{NO})_2\text{SO}_3$.

Potassium dinitrososulphite $\text{K}_2(\text{NO})_2\text{SO}_3$ separates in crystals when nitric oxide is passed over the surface of slightly alkaline potassium sulphite solution in a flask from which air is previously displaced by hydrogen. The dinitrososulphites at once evolve *nitrous* oxide with acids: $\text{K}_2(\text{NO})_2\text{SO}_3 - \text{K}_2\text{SO}_4 + \text{N}_2\text{O}$.

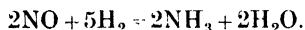
Nitric oxide combines with free oxygen to form red nitrogen dioxide: $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. By passing nitric oxide into liquid oxygen, or by the action of air on solid nitric oxide at -180° , a green solid oxide N_3O_4 is said to be formed. Nitric oxide and oxygen dried with phosphorus pentoxide are said not to combine.

Nitric oxide is the most stable oxide of nitrogen; it begins to decompose into nitrogen and oxygen appreciably only above 1000° , and unless this temperature is reached combustion does not proceed in the gas. A burning taper, burning sulphur, charcoal, and feebly burning phosphorus are extinguished, but brightly burning phosphorus continues to burn brilliantly, a red gas being produced as well as white clouds of phosphorus pentoxide:



A mixture of carbon disulphide vapour and nitric oxide, formed by shaking a few ml. of carbon disulphide in a jar of nitric oxide, when kindled burns with a brilliant blue flame.

A mixture of hydrogen and nitric oxide (or nitric acid vapour, or any oxide of nitrogen except nitrous oxide) when passed over heated platinum is reduced to ammonia:



Nitric oxide is absorbed by concentrated nitric acid to a yellow solution of NO_2 : $2\text{HNO}_3 + \text{NO} = 3\text{NO}_2 + \text{H}_2\text{O}$. With more dilute acid a green ($\text{NO}_2 + \text{N}_2\text{O}_3$) or blue (N_2O_3) solution is formed. Beyond a certain dilution the acid absorbs very little gas.

The composition of *nitric oxide* may be determined by heating a piece of potassium in a confined volume in a bent tube over mercury, or a spiral of iron wire may be heated strongly by an electric current in a measured volume of gas confined by mercury. The oxygen is removed by the potassium or the iron, and after cooling the nitrogen occupies half the original volume of gas. Hence one molecule of nitric oxide contains half a molecule or one atom of nitrogen, and the formula is NO_x . The density of the gas shows that the molecular weight is 30. This contains one atom, or 14 parts of nitrogen, and $30 - 14 = 16$ parts of oxygen, *i.e.* 1 atom of each element, so that the formula is NO . (Nitric oxide does *not* explode with hydrogen when sparked unless previously mixed with an equal volume of nitrous oxide).

The analysis of nitric oxide by heating finely-divided nickel in the gas was carried out by R. W. Gray (1905). The ratio N : O = 14.0085 : 16 was

found. The normal density of the gas was also found to be 1.3402, so that after a correction for compressibility (p. 105) the molecular weight ($O = 16$) is 30.009; or $N = 30.009 - 16 = 14.009$. The apparatus is shown in

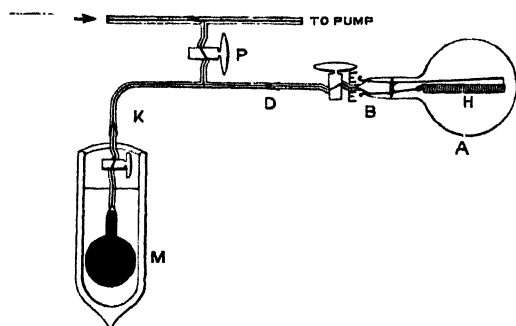


FIG. 291.—Gray's apparatus for determining the composition of nitric oxide.

Fig. 291. The gas was contained in the bulb *A*, which was weighed first empty and then full of gas. The platinum boat *H*, heated by a platinum spiral, contained the nickel. The bulb *M* contained charcoal. After decomposition was complete, the bulb *M* was put in communication with *A* and immersed in liquid air. The nitrogen condensed on the charcoal,

and was weighed. The increase in weight of *A* gave the weight of oxygen which had combined with the nickel: $2NO + 2Ni = N_2 + 2NiO$. The atomic weight of nitrogen found by other methods is 14.008.

Nitrous oxide.—Priestley in 1772 noticed that if nitrous air (NO) is allowed to stand in contact with iron or liver of sulphur (potassium sulphide) it contracts, and the gas ("diminished nitrous air") then supports combustion better than common air, although oxygen has been removed from the nitrous air.

The flame of a taper in the gas is enlarged, as Priestley says "by another flame (extending everywhere to an equal distance from that of the candle, and often plainly distinguishable from it) adhering to it."

Priestley also obtained the gas by the action of diluted nitric acid on zinc or iron. It was carefully examined by Davy in 1799, who prepared it in the pure state by a method discovered by Berthollet in 1785, viz. by heating ammonium nitrate. Davy determined its composition and examined its physiological action. He called it *nitrous oxide*. Its use as an anaesthetic and its peculiar effects ("laughing gas") are well known.

Nitrous oxide is not easily synthesised. Chapman, Goodman and Shepherd (1926) obtained it by passing an electric discharge through nitrogen at low pressure in a tube of fused silica, the walls of which had previously been saturated with oxygen by passing a discharge through that gas at low pressure in the tube.

Nitrous oxide is most conveniently obtained by the decomposition of ammonium nitrate by heat: $NH_4NO_3 = N_2O + 2H_2O$. This gas may contain some nitrogen.

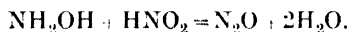
Heat about 50 gm. of pure ammonium nitrate, previously dried at 105° , in a glass retort over wire gauze. The salt melts at 170° (when quite dry;

usually at 165°), and begins to decompose below 200°. The reaction is exothermic : $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O} + 5 \text{ k. cal.}$, and if the salt is heated above 250° it is liable to explode ; before this occurs, nitric oxide, nitrogen, and ammonia are evolved.

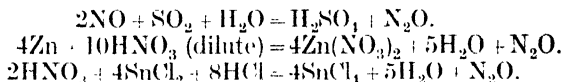
The gas is purified from higher oxides of nitrogen by passing through potassium permanganate solution, from chlorine (derived from ammonium chloride in the ammonium nitrate) and nitric acid vapour by sodium hydroxide solution, and from ammonia by concentrated sulphuric acid, and is collected over warm water or mercury, or by downward displacement.

Nitrous oxide is prepared for use as a mild anaesthetic ; it is carefully purified from chlorine and nitric oxide and liquefied by compression in steel cylinders.

Very pure nitrous oxide is obtained by mixing solutions of equimolecular amounts of hydroxylamine hydrochloride and sodium nitrite, warming gently if necessary :



Nitrous oxide is produced by the reduction of moist nitric oxide by sulphur dioxide or sulphites, or of nitric acid by metals or stannous chloride under special conditions :



A mixture of 1 vol. of concentrated sulphuric acid, 1 vol. of concentrated nitric acid, and 10 vols. of water is said to evolve fairly pure nitrous oxide with zinc.

Properties of nitrous oxide.—Nitrous oxide is a colourless gas, about $1\frac{1}{2}$ times as heavy as air (normal density 1.9777 gm./lit.) with a faint sweetish odour and taste. It is appreciably soluble in water and more soluble in alcohol. The volumes at S.T.P. absorbed are :

Temperature	0°	5°	10°	15°	20°	25°
1 vol. of water	1.3052	1.0954	0.9196	0.7778	0.6700	0.5962
1 vol. of alcohol	4.178	3.844	3.541	3.268	3.025	—

The solution has no action on litmus : nitrous oxide is a neutral oxide and does not behave as the anhydride of hyponitrous acid, although it is formed by its decomposition : $\text{H}_2\text{N}_2\text{O}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$. When cooled to -90° or exposed to pressure (30 atm. at 0° ; 50 atm. at 15°) the gas forms a colourless mobile liquid, b. pt. -88.7° ; the critical temperature is 36.5° , the critical pressure 71.66 atm. It is thus rather easily liquefied, and the liquid exists under pressure at room temperature. The density of the liquid at the b. pt. is 1.26, when cooled in liquid air, or when *rapidly* evaporated (not spontaneously on reducing the pressure, as in the case of liquid carbon dioxide), it forms a snow-like mass, with some transparent crystals, m. pt. -90.8° .

Nitrous oxide supports combustion more vigorously than air, since on decomposition it yields a gas containing one-third its volume of

oxygen, as compared with one-fifth in air: $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$. Decomposition of nitrous oxide begins at 520° , and is complete at 900° . At lower temperatures the principal reaction is $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$, but at 1300° the reaction $2\text{N}_2\text{O} = 2\text{NO} + \text{N}_2$ also occurs. The gas is decomposed by electric sparks, and some nitric oxide is also formed. This gives a gas containing half its volume of oxygen, but does not support combustion so easily as air or nitrous oxide. This is probably because nitrous oxide is more easily decomposed by heat than nitric oxide, which is stable to about 1000° . Combustion in *nitric* oxide, once begun, is more brilliant than in nitrous oxide.

A taper burns in nitrous oxide with a brilliant flame, and charcoal burns, and a glowing chip is rekindled, as in oxygen. (The *dry* gas should be used). Nitrous oxide is distinguished from oxygen by its smell, its greater solubility in water and alcohol, and the fact that it does not produce a red gas with nitric oxide.

Brightly burning phosphorus burns in nitrous oxide with a brilliant flame, forming phosphorus pentoxide and a little red nitrogen dioxide. Feebly burning sulphur is extinguished, but brightly burning sulphur continues to burn vigorously with a double flame. The outer large, flickering, yellow flame corresponds with the reaction $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$, and the inner, bright-blue flame to the reaction $\text{S} + \text{O}_2 = \text{SO}_2$. Sodium and potassium on heating burn in the gas to oxides, and iron wire burns as in oxygen. A hydrogen flame is greatly enlarged in nitrous oxide. The ignition points of hydrogen, ethylene and propylene are lower in nitrous oxide than in oxygen or air, probably owing to the catalytic effect of traces of nitric oxide formed.

Nitrous oxide is an *endothermic* compound ($\text{N}_2 + \frac{1}{2}\text{O}_2 = \text{N}_2\text{O} - 19.7$ k. cal.) and is decomposed into its elements by the shock of exploding mercury fulminate. If mixed with detonating gas ($2\text{H}_2 + \text{O}_2$), nitrous oxide is also completely decomposed on explosion, and this may be used to determine the composition of the gas.

Two vols. of nitrous oxide when mixed with electrolytic gas and exploded leave three volumes of gas (all the electrolytic gas is condensed to liquid water). On treatment with alkaline pyrogallol, 1 vol. of oxygen is absorbed, and 2 vols. of nitrogen are left. Thus $2\text{N}_x\text{O}_y = 2\text{N}_2 + \text{O}_2$, hence $x = 2$ and $y = 1$, and the formula is N_2O . Gay-Lussac and Thenard (1811) determined the composition of nitrous and nitric oxides by heating potassium in a measured volume of the gas confined in a bent tube over mercury. With nitrous oxide, after cooling, an equal volume of nitrogen remained. The gas may also be decomposed by heated iron wire, as in the case of nitric oxide: in this way Jaquered and Bogdan (1904) found that 1 vol. of N_2O gave 1.00686 vols. of N_2 .

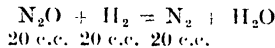
These experiments show that *nitrous oxide contains its own volume of nitrogen*, and the formula is N_2O_x . The density gives the molecular weight 44. But this contains a molecular weight of nitrogen, N_2 , of weight 28, and therefore $44 - 28 = 16$ parts, or one atom of oxygen. The formula is therefore N_2O .

The formula may be found by exploding the gas with hydrogen in a eudiometer (Davy, 1799). If 20 c.c. of nitrous oxide mixed with 20 c.c.

of hydrogen are exploded, 20 c.c. of nitrogen are left. The hydrogen must have combined with 10 c.c. of oxygen to form liquid water, so that 2 vols. of nitrogen are combined in 2 vols. of nitrous oxide with 1 vol. of oxygen, and the formula is N_2O .

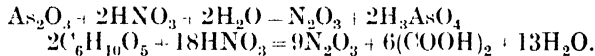
Nitric oxide does not usually explode with hydrogen, but if mixed with an equal volume of nitrous oxide and with hydrogen, both gases explode when sparked.

In an experiment a mixture of 20 c.c. of nitrous oxide, 20 c.c. of nitric oxide, and 40 c.c. of hydrogen was exploded. Thirty c.c. of nitrogen remained. Of this, 20 c.c. must have come from the nitrous oxide :



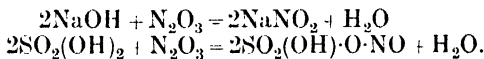
hence the 20 c.c. of nitric oxide gave 30 - 20 = 10 c.c. of nitrogen. Again, 20 c.c. of hydrogen are used up by the nitrous oxide, so that 40 - 20 = 20 c.c. of hydrogen have combined with the oxygen in the 20 c.c. of nitric oxide, which must therefore have been 10 c.c. Thus, 20 c.c. of nitric oxide contain 10 c.c. of nitrogen and 10 c.c. of oxygen, or one molecule contains half a molecule or one atom of nitrogen, and half a molecule or one atom of oxygen. Hence the formula of nitric oxide is NO.

Dinitrogen trioxide.—Red vapours obtained by distilling diluted nitric acid with arsenious oxide or starch, on cooling in a freezing mixture, give a dark-blue volatile liquid, which is dinitrogen trioxide, N_2O_3 :



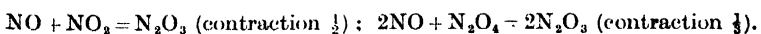
Heat 100 gm. of white arsenic with 80 ml. of nitric acid of sp. gr. 1.35 (56 per cent HNO_3) in a large flask with a long tube connected by a paraffined cork with a glass worm cooled with ice and salt (Fig. 259). A deep-blue liquid condenses, and is collected in a tube in ice and salt. The tube may be sealed to preserve the liquid. *Vapours of higher oxides of nitrogen are dangerously poisonous.*

The red gas is absorbed by sodium hydroxide solution with formation of sodium nitrite, and by concentrated sulphuric acid with formation of nitrososulphuric acid. It thus behaves as if it were nitrous anhydride, N_2O_3 :



The vapour density shows, however, that the gas is a mixture of equal volumes of nitric oxide and nitrogen dioxide, so that N_2O_3 in the gaseous state is almost completely dissociated : $N_2O_3 \rightleftharpoons NO + NO_2$.

Ramsay and Cundall (1885) collected gaseous nitrogen dioxide in a tube over mercury and introduced into it a thin bulb filled with nitric oxide. When the latter was broken there was no change of volume, whereas according to the experimenters there should have been a contraction if N_2O_3 is formed :



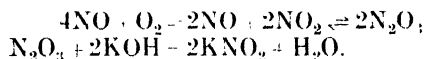
Dixon and Peterkin (1899) pointed out that if there had been no combination an *expansion* of nearly 10 c.c. should have occurred, due to dissociation of N_2O_4 present in the nitrogen dioxide, owing to its dilution with the other gas: $N_2O_4 \rightleftharpoons 2NO_2$. Since there was a contraction of about 0.3 c.c., there must have been reaction leading to diminution of volume, which they assumed to be formation of N_2O_3 . With nitrogen dioxide and an indifferent gas, or with NO above 50°, there was the normal expansion of 10 c.c. The gas obtained by mixing 100 vols. of NO and 100 vols. of nitrogen dioxide (NO_2 and N_2O_4) at 27° they calculated should have the following composition

	N_2O_4 .	NO_2 .	NO.	N_2O_3 .	Total.
Before mixing -	68	32	100	0	200
After mixing -	62	38	94	6	200

According to H. B. and M. Baker (1907), the blue liquid dried by prolonged exposure to phosphorus pentoxide may be volatilised without decomposition, and has a vapour density corresponding with N_2O_3 ; in presence of a trace of moisture it decomposes: $N_2O_3 \rightleftharpoons NO + NO_2$. Other experimenters did not confirm this result.

Liquid dinitrogen trioxide is obtained by the action of nitric oxide on solid nitrogen dioxide cooled in liquid air. It is not oxidised to NO_2 by oxygen below -100° , melts at -102° , and (unless quite dry) begins to decompose at -21° .

A mixture of nitric oxide with oxygen or air, if rapidly made in presence of alkali, is quickly absorbed with formation of nitrite only, and thus behaves as if it contained N_2O_3 :



If the gas mixture is allowed to stand, it is more slowly absorbed by alkali, with formation of both nitrite and nitrate from the nitrogen dioxide formed by the complete oxidation of the nitric oxide:



To 20 c.c. of pure NO in a 3 cm. diameter tube over mercury containing 10 c.c. of concentrated KOH add rapidly 25 c.c. of air. Almost immediate absorption of the red gas occurs and 20 c.c. of N_2 remain. To 10 c.c. of NO in a second tube, without alkali, add 25 c.c. of air, and after 2 minutes add 10 c.c. of potash solution. The red gas is absorbed and 20 c.c. of N_2 remain (Gay-Lussac, 1816).

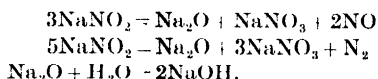
By means of a T-tube admit a *small* amount of NO into a *rapid* stream of air passing into a large flask. Cork the flask and allow it to stand with a piece of white paper behind. Observe the *slow* appearance of the yellow colour due to NO_2 , indicating the time required for the oxidation of NO in dilute gases.

These reactions were thought to show that N_2O_3 is the first product of oxidation of NO and is then further oxidised to NO_2 , but they may be explained by the slowing down of the speed of oxidation of NO to

NO_2 when half the NO is oxidised in the termolecular reaction :
 $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.

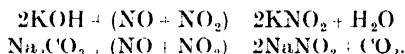
Nitrous acid and nitrites. -- Scheele (1774) found that the residue after heating nitre (potassium nitrate) effervesced with acids and gave a red gas, hence he concluded that it is a salt of a new acid ; it is **potassium nitrite** : $2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2$. The reduction occurs at a lower temperature by fusing potassium or sodium nitrate with lead or copper, extracting with water, filtering from the metallic oxide, and evaporating :
 $\text{NaNO}_3 + \text{Pb} = \text{NaNO}_2 + \text{PbO}$.

A little sodium hydroxide is formed, since nitrites decompose at a high temperature :

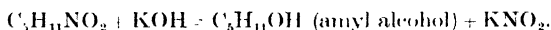


This dissolves lead oxide. Lead hydroxide is precipitated by neutralising with nitric acid. The crystals of **sodium nitrite** are dried at 50° . They have a yellowish colour and usually contain some nitrate. Potassium nitrite may be obtained similarly but does not crystallise well, hence it is precipitated from the solution by alcohol, or is fused and cast into sticks.

Purer nitrites are formed by passing the red gas evolved on heating nitric acid with arsenious oxide into a solution of alkali (sp. gr. 1.38) or carbonate out of contact with air :



Pure potassium nitrite is obtained by decomposing amyl nitrite with alcoholic potash :



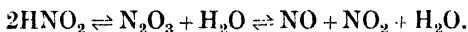
Potassium and sodium nitrites are slightly, and their concentrated solutions markedly, yellow. The solutions are not alkaline when the salts are pure. Sodium nitrite melts at 284° , and 4 parts dissolve in 5 parts of water at 15° . Its crystals are thin flat rhombic prisms, moderately deliquescent : it may be purified by recrystallisation (unlike KNO_2). Potassium nitrite, m. pt. 441° , forms minute short monoclinic prisms containing no water : it is not deliquescent when quite pure, and is soluble in one-third its weight of water.

Barium nitrite is prepared by mixing hot, almost saturated solutions of sodium nitrite and barium chloride, filtering from sodium chloride in a hot-water funnel, and allowing the filtrate to crystallise : $2\text{NaNO}_2 + \text{BaCl}_2 \rightleftharpoons 2\text{NaCl} + \text{Ba}(\text{NO}_2)_2$. The salt is recrystallised and dried over sulphuric acid, when it forms $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$.

Silver nitrite AgNO_2 is obtained as a yellowish-white, sparingly soluble (0.33 gm. in 100 water at 15°) precipitate, when alkali nitrite is added to silver nitrate solution. It is purified by recrystallisation from hot water. Nearly all other nitrites are soluble.

If a dilute acid (even acetic) is added to a nitrite solution, free **nitrous acid** HNO_2 is formed, but this decomposes, nitric oxide and nitrogen

dioxide being liberated. The solution has a pale-blue colour, due to N_2O_3 . The decomposition of nitrous acid in fairly concentrated solutions is probably :



In dilute solutions it decomposes according to the equation :



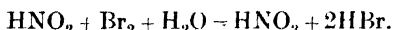
The amount of nitrous acid or N_2O_3 left is never more than a few per cent. A pale-blue pure dilute solution of nitrous acid is obtained by precipitating a solution of barium nitrite with dilute sulphuric acid ; it slowly decomposes, especially on heating or shaking, with evolution of nitric oxide. The free acid can be titrated with sodium hydroxide and alizarin red as indicator. Nitrous acid is rather weak :

$$K_a = [H^+][NO_2^-]/[HNO_2] = 5 \times 10^{-4} \text{ at } 15^\circ.$$

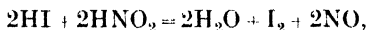
Nitrous acid and nitrites are *reducing* agents : $HNO_2 + O = HNO_3$. They reduce acid permanganate, dichromate, and bromine water, but not alkaline permanganate. They may be estimated in solution by running into excess of warm acidified $N/2$ potassium permanganate, and titrating the excess with standard oxalic acid :



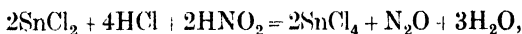
The reaction with bromine water is :



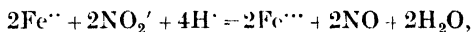
Nitrous acid and nitrites sometimes act as *oxidising* agents : $2HNO_2 = 2NO + O + H_2O$. Iodine is liberated from acidified potassium iodide :



indigo is bleached, stannous chloride is oxidised to stannic chloride :



ferrous salts are oxidised to ferric salts :



sulphur is precipitated from hydrogen sulphide, and sulphur dioxide is oxidised to sulphuric acid. In presence of atmospheric oxygen, NO will reproduce nitrous acid, so that a small amount of nitrous acid may act as a carrier of oxygen.

The liberation of iodine from potassium iodide (blue colour with starch) is a test for nitrous acid or a nitrite in acid solution. Still more delicate tests are (i) the brown colour with a solution of metaphenylenediamine hydrochloride in hydrochloric acid, and (ii) the intense pink colour with a mixture of solutions of sulphanilic acid and α -naphthylamine in acetic acid. These two reactions are used to determine nitrites in water.

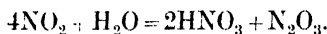
The reagents are prepared as follows : (a) Dissolve 1 gm. metaphenylenediamine in concentrated hydrochloric acid and dilute to 200 ml. (b) Dissolve 1 gm. sulphanilic acid in 10 ml. glacial acetic acid + 50 ml. water and

dilute to 250 ml. Dissolve 0.2 gm. α -naphthylamine in 10 ml. glacial acetic acid + 50 ml. water and dilute to 300 ml. Mix equal volumes before use.

Nitrites detonate violently when heated with thiosulphates or cyanides. A mixture of sulphur, potassium carbonate and nitre, or of nitre and potassium cyanide, detonates violently when heated. These mixtures sometimes cause surprises in qualitative analysis.

Nitrogen dioxide and dinitrogen tetroxide. -If nitric oxide is mixed with oxygen or a gas containing free oxygen, a red gas is produced. This consists mostly of nitrogen dioxide: $2\text{NO} + \text{O}_2 = 2\text{NO}_2$, but below 140° part is associated to form dinitrogen tetroxide: $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$. The oxides N_2O_3 and NO_2 were first clearly distinguished by Gay-Lussac and by Dulong in 1816. Nitrogen dioxide was discovered by Priestley in 1777.

If a dry mixture of 1 vol. of oxygen and 2 vols. of nitric oxide is passed *slowly* through a large bulb so as to allow time for complete oxidation, and then through a spiral tube cooled in a freezing mixture, yellow liquid dinitrogen tetroxide is condensed. But the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ requires time for completion, and if the mixed gas is passed *rapidly* into a cooled tube a green liquid condenses, which is a mixture of dinitrogen tetroxide and blue dinitrogen trioxide formed from the dioxide and unchanged nitric oxide. If the gases are moist the liquid is always green:

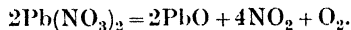


The velocity of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ *decreases* with rise in temperature; at -184° it is 100 times as fast as at 0° .

Nitrogen dioxide is formed by the action of *concentrated* nitric acid on copper or bismuth:



It is usually prepared by the decomposition of lead nitrate by heat:



The gas may be passed through a phosphorus pentoxide tube to dry it, and passed into a spiral condenser cooled by a freezing mixture (Fig. 259), the liquid formed being collected in a cooled tube, which may be sealed. *The vapour is poisonous.*

Heat dry powdered lead nitrate in a hard glass tube, and pass the gas evolved through a U-tube cooled in a mixture of ice and salt (Fig. 292). A yellow liquid collects. Hold a glowing chip over the exit of the collecting tube: it bursts into flame, showing that oxygen is also evolved.

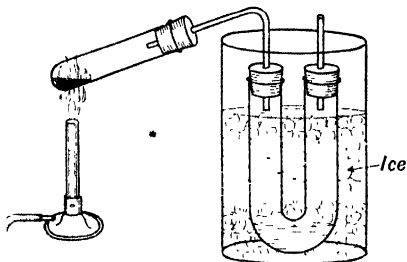
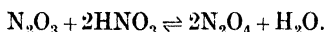


FIG. 292. Preparation of nitrogen dioxide from lead nitrate.

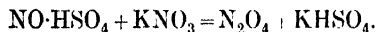
Pour the N_2O_4 on crushed ice in a test tube. A deep-blue layer rich in N_2O_3 separates: $2N_2O_4 + 2H_2O \rightleftharpoons 2HNO_2 + 2HNO_3 \rightleftharpoons N_2O_3 + 2HNO_3 + H_2O$ (Fritsche, 1840).

A more convenient method of preparing nitrogen dioxide is by the action of nitric acid and phosphorus pentoxide on a mixture of nitrous anhydride and nitrogen dioxide, obtained by distilling arsenious oxide with a mixture of concentrated nitric acid and half its weight of concentrated sulphuric acid (Ramsay and Cundall, 1890):



To the blue liquid obtained by distillation add excess of P_2O_5 and fuming nitric acid drop by drop until the colour changes to yellow. The mixture should be kept well cooled in a freezing mixture. Distil and collect as before.

The best method of preparation is to heat nitrososulphuric acid ("chamber crystals") with dry potassium nitrate:



Pass sulphur dioxide *slowly* into *well cooled* fuming nitric acid in a retort until the liquid becomes a pasty mass of crystals of nitrososulphuric acid. Add dry powdered potassium nitrate, stir well, stopper the retort, heat gently and collect the N_2O_4 as above.

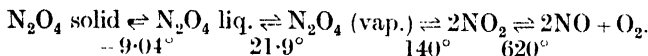
Properties of nitrogen dioxide.—Dinitrogen tetroxide in a good freezing mixture solidifies to pale-yellow, nearly colourless crystals melting at -9.04° to a honey-yellow liquid (the liquid supercools strongly). The solid probably consists almost entirely of N_2O_4 , which appears to be colourless. The liquid at the melting point already contains some NO_2 , which is strongly coloured. On warming, the colour deepens; at 10° it is yellow, at 15° orange, and at 21.9° it is reddish-brown, and the liquid boils, giving a red vapour. The colour of the vapour darkens on further heating, as may be seen by comparing two bulbs containing it, one at the ordinary temperature: at 40° it is almost black.

The colour change accompanies a decrease in density (reduced to S.T.P.) to 140° , when the density becomes constant and corresponds with NO_2 . The intermediate densities correspond with the dissociation: $N_2O_4 \rightleftharpoons 2NO_2$. Values for 1 atm. pressure (density referred to oxygen = 16) are:

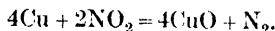
Temperature	Density	Dissociation
21.9° (b. pt.)	39.81	15.7
26.7	38.3	20.1
60.2	30.1	52.8
100.1	24.3	89.3
135.0	23.1	99.1
140.0	22.96	100.0

Above 140° , the density decreases and the colour becomes paler, owing to dissociation: $2NO_2 \rightleftharpoons 2NO + O_2$, until at 620° the gas is

colourless and dissociation is complete. Recombination occurs on cooling :

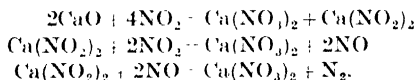


The composition of nitrogen dioxide is found by passing it over copper heated to *bright redness* (otherwise NO is formed) :



Nitrogen dioxide vapour is a supporter of combustion : it kindles a glowing chip and strongly burning phosphorus and carbon burn in it. Potassium inflames spontaneously in the gas, heated sodium burns in it, and a spiral of heated iron wire combines with the oxygen, leaving half the volume of nitrogen : $2\text{NO}_2 = \text{N}_2 + 2\text{O}_2$. The composition of the gas may be determined in this way. Tin is oxidised to dioxide, carbon monoxide to carbon dioxide at the ordinary temperature : hydrogen sulphide deposits sulphur and the nitrogen dioxide is reduced to nitric oxide : $\text{NO}_2 + \text{H}_2\text{S} = \text{NO} + \text{H}_2\text{O} + \text{S}$. A mixture of the gas and hydrogen is reduced to ammonia on passing over heated platinum : $2\text{NO}_2 + 7\text{H}_2 = 2\text{NH}_3 + 4\text{H}_2\text{O}$.

Nitrogen dioxide is absorbed by concentrated sulphuric acid to form nitrososulphuric acid and nitric acid, and since these decompose each other, a state of equilibrium is attained : $\text{N}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_2(\text{OH})\cdot\text{O}\cdot\text{NO} + \text{HNO}_3$. The gas is absorbed by alkalis with formation of a mixture of nitrite and nitrate : $2\text{KOH} + \text{N}_2\text{O}_4 = \text{KNO}_2 + \text{KNO}_3 + \text{H}_2\text{O}$. Baryta becomes incandescent at 200° in the gas. Quicklime, and oxides of zinc, aluminum, and lead, absorb the gas on heating, but free nitrogen and nitric oxide are liberated with quicklime (Oswald, 1914), from the calcium nitrite first produced (Partington and Williams, 1924) :



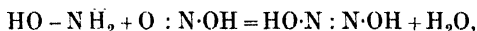
Nitrogen dioxide reacts with copper forming cuprous oxide, which then absorbs a further quantity of the gas : $2\text{Cu} + \text{NO}_2 = \text{Cu}_2\text{O} + \text{NO}$ (Park and Partington, 1924) : the so-called "nitro-copper" produced is not a definite substance.

Hyponitrous acid.—Divers (1871), by reducing a solution of sodium nitrite or nitrate with sodium amalgam, neutralising with acetic acid, and adding silver nitrate, obtained a *yellow* precipitate of silver hyponitrite $\text{Ag}_2\text{N}_2\text{O}_2$. Sodium hyponitrite $\text{Na}_2\text{N}_2\text{O}_2$ is best prepared by reducing a concentrated solution of sodium nitrite with liquid sodium amalgam.

Excess of sodium amalgam is added to a solution of 25 gm. of sodium nitrite in 75 ml. of water : the reaction evolves heat, and by the prolonged action of the amalgam the hydroxylamine formed is removed. The resulting ammonia is removed by exposing the solution over concentrated sulphuric acid in a vacuum desiccator. Granular crystals of sodium hypo-

nitrite, $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$, slowly separate. They are washed with alcohol and again exposed in the vacuum desiccator, when they fall to a white powder of anhydrous salt, $\text{Na}_2\text{N}_2\text{O}_2$, stable in air.

Hyponitrous acid is formed in small quantities by the action of nitrous acid on hydroxylamine (Wislicenus, 1893):



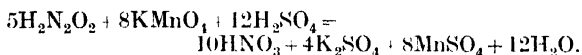
but most of it decomposes into water and nitrous oxide: $\text{H}_2\text{N}_2\text{O}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$.

To a solution of hydroxylamine sulphate add sodium nitrite solution. Heat rapidly to 60° , then add silver nitrate solution. A *canary-yellow* precipitate of silver hyponitrite is formed. If the conditions are not correct, a yellowish-white precipitate of silver nitrite is obtained.

Sodium hyponitrite is formed in poor yield by warming sodium hydroxylamine sulphate with sodium hydroxide: $2\text{HO} \cdot \text{NH} \cdot \text{SO}_3\text{Na} + 4\text{NaOH} = \text{Na}_2\text{N}_2\text{O}_2 + 2\text{Na}_2\text{SO}_3 + 4\text{H}_2\text{O}$. The products formed by passing nitric oxide into a solution of sodium in liquid ammonia, or the sodium compound of pyridine suspended in benzene, have been supposed to be sodium hyponitrite: $2\text{Na} + 2\text{NO} = \text{Na}_2\text{N}_2\text{O}_2$.

If silver hyponitrite is added gradually to an ether solution of hydrogen chloride in absence of moisture, and the filtered solution evaporated *in vacuo*, crystalline laminae of free hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$, are formed, which explode feebly when dry. The solution decomposes with evolution of nitrous oxide: $\text{H}_2\text{N}_2\text{O}_2 = \text{H}_2\text{O} + \text{N}_2\text{O}$.

Hyponitrites in acid solution reduce permanganate:



In alkaline solution a nitrite is formed. They are very stable towards reducing agents.

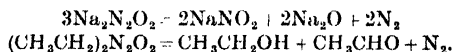
The formula $\text{H}_2\text{N}_2\text{O}_2$ of the acid is supported by the following evidence:

1. Acid and normal salts $\text{Ba}(\text{HN}_2\text{O}_2)_2$ and BaN_2O_2 are known.
2. The lowering of freezing point of the solution of the acid corresponds with $\text{H}_2\text{N}_2\text{O}_2$.
3. By the action of ethyl iodide on silver hyponitrite, ethyl hyponitrite is obtained, the molecular weight of which corresponds with the formula $(\text{C}_2\text{H}_5)_2\text{N}_2\text{O}_2$.
4. The esters have no dipole moment, hence the formula of hyponitrous acid is the *trans*-modification, the two N—OH groups being on opposite sides

of the double bond:

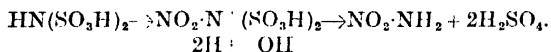
$$\begin{array}{c} \text{HO} - \text{N} \\ \parallel \\ \text{N} - \text{OH}. \end{array}$$

The salts and esters decompose on heating:



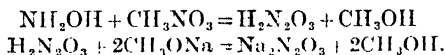
By the action of sodium on NaNO_2 dissolved in liquid ammonia, yellow sodium hyponitrite Na_2NO_2 is formed, which explodes in moist air (Maxted, 1917).

Nitramide.—By the nitration of potassium imidosulphonate under special conditions, and hydrolysis, an isomer of hyponitrous acid called nitramide is formed :



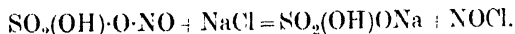
Thiele and Lachmann represented it as NH_2NO_2 , i.e. the amide of nitric acid, or as $\text{HN}:\text{NO}(\text{OH})$, i.e. the imide of nitric acid, $\text{NO}_2 \cdot \text{OH}$ (one oxygen atom being replaced by $=\text{NH}$). Nitramide is a white crystalline solid, more stable than hyponitrous acid but readily decomposing into water and nitrous oxide. It has feebly acidic properties and forms a mercuric salt $\text{HgN} \cdot \text{NO}_2$.

Hyponitric acid.—If methyl nitrate is added to a solution of free hydroxylamine and sodium methoxide in methyl alcohol, the sodium salt of hyponitric acid $\text{Na}_2\text{N}_2\text{O}_3$ is obtained :



This is slowly decomposed by boiling with water : $2\text{Na}_2\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NaNO}_2 + \text{N}_2\text{O} + 2\text{NaOH}$. The solid salt when heated decomposes into nitrite and hyponitrite : $2\text{Na}_2\text{N}_2\text{O}_3 = \text{Na}_2\text{N}_2\text{O}_2 + 2\text{NaNO}_2$. On acidifying the salt, the free acid liberated at once decomposes into nitric oxide and water : $\text{H}_2\text{N}_2\text{O}_3 = 2\text{NO} + \text{H}_2\text{O}$.

Nitrosyl chloride.—A mixture of 1 vol. of concentrated nitric acid and 4 vols. of concentrated hydrochloric acid was called by the alchemists *aqua regia* because it dissolves gold, "the king of metals"; it owes this property to the presence of free chlorine. On warming *aqua regia*, it evolves an orange-yellow mixture of chlorine and nitrosyl chloride (Gay-Lussac, 1848) : $\text{HNO}_3 + 3\text{HCl} = \text{NOCl} + \text{Cl}_2 + 2\text{H}_2\text{O}$. The gas is dried by calcium chloride and passed into concentrated sulphuric acid : chlorine passes on, whilst nitrosyl chloride is absorbed as nitrososulphuric acid : $\text{NOCl} + \text{SO}_2(\text{OH})_2 = \text{SO}_2(\text{OH}) \cdot \text{O} \cdot \text{NO} + \text{HCl}$. (The nitrososulphuric acid can be prepared in other ways : see below). When nitrososulphuric acid is warmed with sodium chloride, pure nitrosyl chloride is evolved :



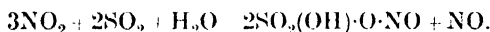
Nitrosyl chloride is formed by direct combination of nitric oxide and chlorine, more rapidly in presence of animal charcoal at $40^\circ - 50^\circ$: $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$; and since it is the acid chloride of nitrous acid, by the action of phosphorus pentachloride on potassium nitrite : $\text{PCl}_5 + \text{KNO}_2 = \text{NOCl} + \text{POCl}_3 + \text{KCl}$.

Nitrosyl chloride is an orange-yellow gas with a suffocating smell, condensing to a ruby-red liquid, b. pt. -5.5° , density 1.4 at -12° , forming in liquid air a lemon-yellow solid, red at the m. pt. -61.5° .

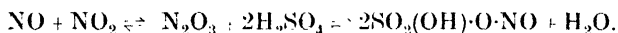
It is readily decomposed by water and alkalis: $\text{NOCl} + 2\text{KOH} = \text{KNO}_2 + \text{KCl} + \text{H}_2\text{O}$. It has no action on gold or platinum, but attacks mercury and most other metals: $2\text{Hg} + 2\text{NOCl} = \text{Hg}_2\text{Cl}_2 + 2\text{NO}$. It is stable, but dissociates above 700° : $2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$. It forms compounds with many metallic chlorides, e.g. $\text{ZnCl}_2 \cdot \text{NOCl}$; $\text{FeCl}_3 \cdot \text{NOCl}$; with MnCl_2 and FeCl_2 , the compounds $\text{MnCl}_2[\text{NO}]$ and $\text{FeCl}_2[\text{NO}]$ are formed.

Nitrosyl bromide, NOBr , a blackish-brown liquid, b. pt. -2° , is formed by passing nitric oxide into bromine at -15° . At the ordinary temperature NOBr_3 is formed. **Nitrosyl fluoride**, NOF , a gas, b. pt. -59.9° , m. pt. -132.5° , is formed by the reaction $\text{NOCl} + \text{AgF} = \text{NOF} + \text{AgCl}$. **Nitrosyl perchlorate**, NOClO_4 , is a solid formed by passing $\text{NO} + \text{NO}_2$ into very concentrated perchloric acid.

Nitrosyl hydrogen sulphate or **nitrososulphuric acid**.—This compound, which is formulated as $(\text{NO})\text{HSO}_4$ or $\text{SO}_2(\text{OH}) \cdot \text{O} \cdot \text{NO}$, supposed to be formed as an intermediate stage (*chamber crystals*) in the lead chamber process, can be obtained in a number of ways. It was obtained by Clement and Desormes in 1806 by the interaction of oxides of nitrogen, sulphur dioxide, and a regulated amount of moisture (p. 475):

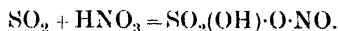


It is formed on passing the red vapours from arsenic trioxide and nitric acid (p. 549) into cooled concentrated sulphuric acid:



Nitrososulphuric acid is violently decomposed by water, with effervescence, evolving red fumes, so that the reaction is reversible. It dissolves in concentrated sulphuric acid and in sulphuric acid containing not more than 35 per cent of water, but in more dilute acid decomposition occurs, and the nitrogen compounds are then almost completely expelled on heating.

Pure nitrososulphuric acid is best prepared by passing sulphur dioxide slowly into well-cooled fuming nitric acid (containing oxides of nitrogen), and draining the white crystals so formed on a porous tile in a desiccator:



The crystals melt with decomposition at 73° and white crystalline **nitrosyl disulphate**, $(\text{NO})_2\text{S}_2\text{O}_7$ or $\text{O}(\text{NO} \cdot \text{O} \cdot \text{SO}_2)_2$ is formed, m. pt. 217° , b. pt. 360° .

Nitrosyl disulphate is more conveniently prepared by the action of nitric oxide on sulphur trioxide at 200° : $3\text{SO}_3 + 2\text{NO} = (\text{NO})_2\text{S}_2\text{O}_7 + \text{SO}_2$, or by the action of liquid sulphur dioxide and nitrogen dioxide in a sealed tube: $2\text{SO}_2 + 3\text{NO}_2 = (\text{NO})_2\text{S}_2\text{O}_7 + \text{NO}$.

Higher oxygen compounds of nitrogen.—By the action of a silent discharge on a mixture of nitrogen and oxygen, Hautefeuille and Chappuis (1881–2) obtained a higher oxide of nitrogen which they supposed was **dinitrogen hexoxide** N_2O_6 , the gas having a characteristic absorption spectrum.

It forms an oxidising solution with water, supposed to contain pernitric acid: $N_2O_6 + H_2O = HNO_4 + HNO_3$. Raschig (1904) found that a mixture of sodium nitrite solution and hydrogen peroxide liberates bromine from potassium bromide solution, which neither does separately, and supposed that pernitric acid is formed. According to Cleu (1935) the oxidising substance is **pernitrous acid** $O=N-O-OH$ (isomeric with nitric acid).

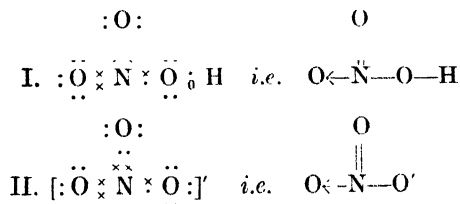
Structure of oxides and oxyacids of nitrogen.—The nitrous oxide molecule is linear and has two atoms of nitrogen adjacent: its formula may be written $:\ddot{N}::N::\ddot{O}:$ or $N \leftarrow N = O$. The structure of nitric oxide must involve an odd electron and may be written as a resonance hybrid of $:\ddot{N}::\ddot{O}:$ and $:\ddot{N}::\dot{O}:$ or with a three-electron bond $:\ddot{O}::\dot{N}:$ (Pauling, 1931). The nitrogen dioxide molecule also contains an odd electron and may be formulated as a resonance hybrid of $:\ddot{O}::N::\ddot{O}:$ and $:\ddot{O}:N::\ddot{O}:$ or of $:\ddot{O}::\dot{N}::\ddot{O}:$ and $:\ddot{O}:\dot{N}::\ddot{O}:$ and the molecule is probably bent. Dinitrogen tetroxide appears to have

a link between the two nitrogens
$$\begin{array}{c} O & & O \\ & \diagdown & / \\ & N-N & \\ & / & \diagdown \\ O & & O \end{array} \quad \text{or} \quad \begin{array}{c} :\ddot{O}::N::\ddot{O}: \\ \quad \quad \quad \cdot \\ :\ddot{O}::N::\ddot{O}: \end{array}$$

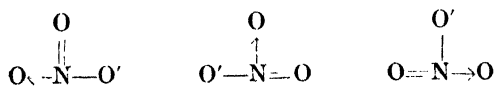
the bonds to oxygen being equalised by resonance; or it may be nitrosyl nitrate $O_3N \cdot NO$. The structure of dinitrogen trioxide may be $O=N \cdot O \cdot N=O$

or $O_2N \cdot NO$. Dinitrogen pentoxide is formulated as
$$\begin{array}{c} O & & O \\ & \diagdown & / \\ & N-O-N & \\ & / & \diagdown \\ O & & O \end{array}$$
 or

$$\begin{array}{c} :\ddot{O}: & :\ddot{O}: \\ :\ddot{O}::N::\ddot{O}::N::\ddot{O}: & \text{by analogy with the formula of nitric acid (see} \\ & \text{below). The electronic formulae of nitric acid (I) and of the nitrate ion} \\ & \text{(II) may be written:} \end{array}$$



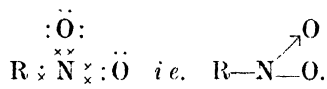
but the three bonds between oxygen and nitrogen (which are all of different types in the above formulae) are levelled out by resonance, e.g. among the structures:



so that the bonds become identical.

The nitrate ion in solid salts is shown by X-rays to be a flat equilateral triangle with the nitrogen in the centre and the three oxygens at the vertices (cf. the carbonate and sulphite ions, p. 470).

Nitrous acid may be formulated as $\text{H} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \overset{\times\times}{\underset{\times\times}{\text{N}}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} i.e. \text{H}-\text{O}-\text{N}=\text{O}$, the nitrite ion being $[\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}]^-$. The H atom in the acid, or the radical R in the esters (*e.g.* $\text{C}_2\text{H}_5\text{NO}_2$, ethyl nitrite), is directly attached to oxygen, since the esters on reduction yield alcohol and ammonia (with some hydroxylamine): $\text{R}\cdot\text{O}\cdot\text{N}::\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} + 6\text{H} = \text{ROH} + \text{NH}_3 + \text{H}_2\text{O}$. In the *nitro-compounds* (which are derivatives of *nitric acid*), *e.g.* $\text{C}_2\text{H}_5\text{NO}_2$ nitroethane, isomeric with nitrites, and formed by the action of silver nitrite on alkyl iodides, the radical is directly attached to nitrogen, since on reduction they yield amines: $\text{R}\cdot\text{NO}_2 + 6\text{H} = \text{R}\cdot\text{NH}_2 + 2\text{H}_2\text{O}$. In the nitro-group, $-\text{NO}_2$, one oxygen is attached by a double bond and the other by a coordinate link, with resonance, as in nitric acid:



Nitrogen never has a covalency greater than four, the old formulæ involving quinevalent nitrogen being incorrect. Silver and mercurous nitrites are pale yellow solids and may have the nitro-group structure.

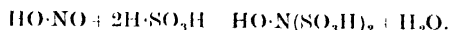
Nitrogen sulphides.—Nitrogen sulphide N_4S_4 is an orange-red crystalline solid obtained by the action of dry ammonia on a solution of sulphur chloride and chlorine in benzene: $16\text{NH}_3 + 6\text{SCl}_2 = \text{N}_4\text{S}_4 + 2\text{S} + 12\text{NH}_4\text{Cl}$, or on thionyl chloride, or by the action of sulphur on liquid ammonia, $10\text{S} + 4\text{NH}_3 \rightleftharpoons \text{N}_4\text{S}_4 + 6\text{H}_2\text{S}$. It melts at 178° , is explosive on percussion; and is decomposed by hot water. It combines with chlorine to form a tetrachloride $\text{N}_4\text{S}_4\text{Cl}_4$, and reacts with S_2Cl_2 to form **thiotritiazyl chloride** $\text{N}_3\text{S}_4\text{Cl}$, which is converted by nitric acid into a crystalline nitrate $\text{N}_3\text{S}_4\cdot\text{NO}_3$. The molecular weight of nitrogen sulphide in solution corresponds with the formula N_4S_4 ; its structure is not known. A blue modification of N_4S_4 is obtained by sublimation of the ordinary form over silver gauze. Nitrogen pentasulphide N_2S_5 is formed as a deep-red liquid, m. pt. $10^\circ - 11^\circ$, when N_4S_4 is heated with carbon disulphide in a sealed tube at 100° . It decomposes on heating.

Sulphonic acids of hydroxylamine and ammonia.—The following compounds are all sulphonic acid derivatives of hydroxylamine, in which H is substituted by $-\text{SO}_2\cdot\text{OH}$:

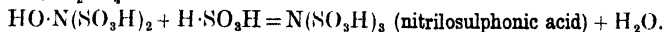
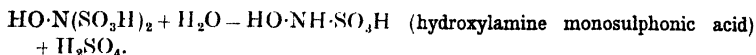
Hydroxylamine		
HO·NH ₂		
HO·NH(SO ₂ H)	HO·N(SO ₂ H) ₂	HSO ₂ ·O·N(SO ₂ H) ₂
H. monosulphonic acid	H. disulphonic acid	H. trisulphonic acid
SO ₂ H·O·NH ₂	SO ₂ H·O·NH(SO ₂ H)	
H. <i>iso</i> -monosulphonic acid	H. <i>iso</i> -disulphonic acid	

Hydroxylamine mono- and disulphonates are formed by the action of nitrites on acid sulphites, as described on p. 524.

The first product appears to be hydroxylamine disulphonic acid :

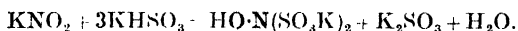


This may undergo hydrolysis or further sulphonation :

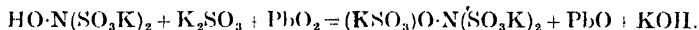


These substances are intermediate products in the oxidation of sulphurous to sulphuric acid by means of nitrous acid.

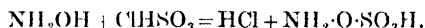
By the action of KNO_2 on KHSO_3 in solution potassium hydroxylamine disulphonate is formed :



On adding lead dioxide the potassium salt of hydroxylamine trisulphonic acid is formed (Fremy, 1845 ; Haga, 1904) :

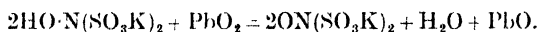


With very dilute acid this loses one SO_3K attached to nitrogen, giving a salt of hydroxylamine *iso*-disulphonic acid $\text{KSO}_3\cdot\text{O}\cdot\text{NH}\cdot\text{SO}_3\text{K}$ (Raschig, Haga, 1906). Hydroxylamine *iso*-monosulphonic acid is obtained by the action of chlorosulphonic acid on hydroxylamine salts (Sommer, 1914) :

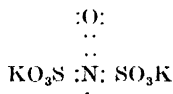


It is the amide of Caro's acid and has oxidising properties, liberating iodine from KI.

By oxidising a warm solution of potassium hydroxylamine disulphonate with lead dioxide, a bluish-violet solution of potassium nitrosodisulphonate, $\text{ON}(\text{SO}_3\text{K})_2$ is formed :



The blue solution is paramagnetic and probably contains the free radical with an odd electron :



but the golden-yellow needles deposited from it are diamagnetic and hence probably dimeric $[\text{ON}(\text{SO}_3\text{K})_2]_2$.

The action of sulphur dioxide on nitrosulphuric acid ("chamber crystals") produces an unstable purple liquid which Raschig supposed to

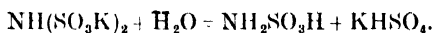
contain nitrosulphuric acid, $\text{HO}\cdot\text{N}\cdot\text{SO}_3\text{H}$, which readily decomposes with evolution of nitric oxide : $\text{H}_2\text{SNO}_3 = \text{H}_2\text{SO}_4 + \text{NO}$. A purple ferrous salt is formed when nitric oxide is passed into a solution of ferrous sulphate in concentrated sulphuric acid, and seems to be the cause of the purple colour formed in the "brown ring test" when only small amounts of nitrates are present. Manchot regarded the purple ferrous compound as a nitroso-

compound $[\text{Fe}(\text{NO})]\text{SO}_4$, and Hantzsch regarded the purple acid as a hydronitroso-salt $[\text{NOH}]\text{HSO}_4$ formed by reduction of $[\text{NO}]\text{HSO}_4$.

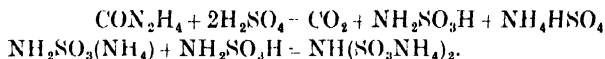
Nitrosulphonic acid, $\text{N}(\text{SO}_3\text{H})_3$, is a derivative of ammonia; crystals of the potassium salt are formed by the reaction between concentrated solutions of potassium disulphite and nitrite:



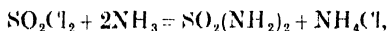
On boiling its salts for a short time with water, they form salts of **imido-disulphonic acid**, $\text{NH}(\text{SO}_3\text{H})_2$: $\text{N}(\text{SO}_3\text{K})_3 + \text{H}_2\text{O} = \text{NH}(\text{SO}_3\text{K})_2 + \text{KHSO}_4$. On further hydrolysis, salts of **amidosulphonic acid**, $\text{NH}_2\cdot\text{SO}_3\text{H}$, are formed:



Amidosulphonic acid (or *sulphamic acid*) is obtained by heating urea with excess of 100 per cent sulphuric acid at 140° ; with equimolecular amounts, imidodisulphonic acid is obtained (Baumgarten, 1936):



Sulphamide $\text{SO}_2(\text{NH}_2)_2$ and **sulphimide**, existing in a trimeric form, $(\text{SO}_2\text{NH})_3$, are formed by the action of ammonia gas on a solution of sulphuryl chloride in benzene:



and by heating sulphamide at 180° till ammonia is no longer evolved:



They form silver compounds $\text{SO}_2(\text{NHAg})_2$ and $[\text{SO}_2(\text{NAg})]_3$.

CHAPTER XXXI

PHOSPHORUS

History.—Brand, of Hamburg, by distilling evaporated urine obtained phosphorus (Greek *phos* light, *phero* I bear) in 1674-5; the phosphate in urine on heating forms sodium metaphosphate and this is reduced on strong heating with carbon (from charred organic matter): $4\text{NaPO}_3 + 5\text{C} \rightarrow \text{Na}_4\text{P}_2\text{O}_7 + 5\text{CO} + 2\text{P}$. Brand made known his process to Krafitt, who showed phosphorus at the Court of Charles II in 1677. There it was seen by Boyle, who was told by Krafitt that it was obtained from a human source. Boyle (who called it *noctiluca*) rediscovered it by distilling evaporated urine with sand, and published the preparation in 1680. Kunckel in 1676 had independently rediscovered phosphorus. Gahn about 1770 discovered calcium phosphate in bones, and Scheele prepared phosphorus from bone-ash. The process formerly used on the large scale (see below) for the preparation from bone-ash was devised by Scheele in 1777.

Occurrence.—Phosphorus always occurs combined, the average percentage in the lithosphere being 0.157 and in ordinary soil 0.1 per cent. The primary minerals are probably *apatite* $3\text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$ and *chlorapatite* $3\text{Ca}_3(\text{PO}_4)_2, 3\text{CaCl}_2$, which are hard and practically insoluble in dilute acids. From them, secondary deposits of *calcium phosphate* $\text{Ca}_3(\text{PO}_4)_2$ have been formed by weathering, although some consist of fossil bones. Phosphorus also occurs in meteorites.

The "soft phosphates", e.g. *coprolites* (calcium phosphate of fossil excreta), and *Charleston phosphate* (27 per cent P_2O_5) from river beds in South Carolina, are easily decomposed by sulphuric acid. "Hard" varieties are the Spanish minerals *estramadurite* (33 per cent P_2O_5) and *sombrerite* (35 per cent P_2O_5). *Redonda phosphate* (35-40 per cent P_2O_5), a cheap and rich ore from the West Indies, is aluminium phosphate AlPO_4 . *Wavellite* is basic aluminium phosphate $4\text{AlPO}_4, 2\text{Al}(\text{OH})_3, 9\text{H}_2\text{O}$, and *vicianite* is ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2, 8\text{H}_2\text{O}$. The richest phosphate deposits are in North Africa and Florida.

Phosphorus compounds occur in vegetable and animal tissues, especially in seeds in which they are concentrated in the germ (cereal grains, except rice, contain 0.4 per cent of P). Yolk of eggs, nerves and brain, and bone-marrow contain fatty esters of phosphoric acid (*lecithins* or *glycero-phosphates*).

In order to repair tissue waste and provide phosphates for bones, phosphorus compounds are essential in foods. Plants take them from the soil as

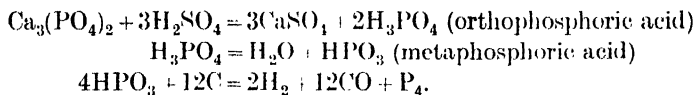
calcium phosphate, and bone meal and calcium superphosphate are used as fertilisers.

Fresh bones contain about 58 per cent (ivory 67 per cent) of calcium phosphate with some calcium carbonate, fats, and organic matter containing nitrogen. Charred bones (animal charcoal) are used in decolorising sugar syrup. When no longer active they are burnt to *bone-ash* containing about 80 per cent of calcium phosphate, with calcium carbonate and a little fluoride.

Preparation.—Phosphorus is obtained by reducing phosphoric acid or a metal phosphate. Since the oxide P_2O_5 is stable and strongly exothermic: $2P + \frac{5}{2}O_2 = P_2O_5 + 360 \text{ k. cal.}$, an energetic reducing agent or a high temperature is required, and silica is usually added to form a silicate with the metal. On the small scale aluminium may be used with sodium metaphosphate and silica: $6NaPO_3 + 3SiO_2 + 10Al = 3Na_2SiO_3 + 5Al_2O_3 + 6P$, and on the large scale calcium phosphate, carbon and silica in the electric furnace.

Mix 1 gm. of powdered sodium metaphosphate, 0.5 gm. of aluminium powder and 3 gm. of fine white sand, all being dry. Heat strongly in a hard glass tube in a current of dry hydrogen. Phosphorus distils and condenses in the cool part of the tube.

In the old process for making phosphorus, bone-ash was decomposed by hot 60 per cent sulphuric acid to form insoluble calcium sulphate and phosphoric acid. The phosphoric acid was filtered, evaporated, mixed with powdered coke and distilled in fireclay retorts at a bright-red heat:



Phosphorus is now made by the direct reduction of a phosphate by carbon in presence of silica (Wöhler, 1829) at a high temperature in the electric furnace (Readman, Parker and Robinson process, 1888). This method can be used with "hard" phosphates, since the mineral is not treated with acid.

A mixture of phosphate, sand (or crushed quartz) and coke is fed into a closed electric furnace provided with an outlet above for gas and phosphorus vapour, a slag hole below, and an adjustable carbon electrode between which and the carbon base an electric arc is struck (Fig. 293).

The phosphate is decomposed by silica at 1150° : $Ca_3(PO_4)_2 + 3SiO_2 = 3CaSiO_3 + P_2O_5$. The calcium silicate forms a molten slag. The phosphorus pentoxide vapour is reduced by carbon at about 1500° , forming carbon monoxide and phosphorus vapour: $P_2O_5 + 5C = 2P + 5CO$. The cooled gas is passed over water in condensers when crude phosphorus separates. The dark-coloured product is purified by melting under chromic acid solution, when some impurities oxidise and dissolve and others

separate as a scum. The liquid phosphorus may be filtered by pressing through charmois leather. The colourless phosphorus is cast into wedges (about 2 lb.) in tin moulds, or into sticks by running the liquid into glass tubes cooled in water and drawing out the stick at the other end.

Most of the phosphorus made is used in the manufacture of matches. Some is used in making phosphor-bronze and incendiary and smoke bombs, as a poison for rats, and in the preparation of phosphorus trichloride, pentachloride, and pentoxide.

Phosphorus exists in two main allotropic forms: *white phosphorus* (sometimes called "yellow" phosphorus although it is quite colourless when pure) and *red phosphorus*, which is the only stable form.

White phosphorus.—Ordinary white phosphorus is a translucent white solid like wax, density 1.83. On exposure to light it rapidly becomes yellow. It is soft enough at the ordinary temperature to be cut with a knife—an operation which should always be performed under water. Below 5.5° it is brittle and the crystalline structure is seen after etching with nitric acid. Large transparent crystals of the cubic system, usually rhombdodecahedra, with a play of colours like diamonds are formed by the slow sublimation of phosphorus in a vacuum tube, one end being kept cool by a moist cloth. The tube is kept in the dark, since on exposure to light the crystals become red and opaque.

White phosphorus is kept in bottles under water on account of the ease with which it takes fire in air. It has a low melting point (44°). It boils at 287° yielding a colourless vapour the density of which corresponds with P_4 . Above 700° the density decreases, indicating partial dissociation: $P_4 \rightleftharpoons 2P_2$. At very high temperatures dissociation into atoms occurs: $P_2 \rightleftharpoons 2P$.

White phosphorus is very sparingly soluble in water but is soluble in benzene, turpentine, olive oil, sulphur chloride, phosphorus trichloride, and especially in carbon disulphide. The elevation of boiling point of the latter solvent gives a molecular formula P_4 agreeing with that of the vapour. On evaporation out of contact with air the solution in carbon disulphide deposits crystals. By shaking melted white phosphorus under a cold solution of urea it forms a fine powder.

A characteristic property of white phosphorus is the ease with which it undergoes spontaneous oxidation when exposed to air at the ordinary

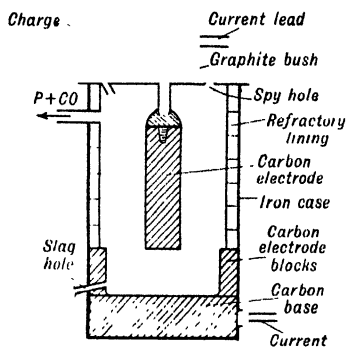


FIG. 293.—Electric furnace for phosphorus.

temperature, accompanied by a green glow or phosphorescence. If warmed to about 50° it inflames in dry air and burns with a white flame, forming white fumes of the pentoxide P_2O_5 . It inflames spontaneously in chlorine, explodes violently in contact with liquid bromine, and inflames in contact with solid iodine. It dissolves slowly in concentrated nitric acid to form phosphoric acid, and in hot alkali hydroxide solution with evolution of phosphine PH_3 .

Phosphorus does not burn when heated in pure oxygen dried with phosphorus pentoxide (Baker, 1888). Finely divided white phosphorus inflames spontaneously in air, and melted white phosphorus burns under water in contact with oxygen.

Pour a solution of phosphorus in carbon disulphide on a piece of blotting-paper supported on a tripod. The solvent rapidly evaporates and the finely divided phosphorus catches fire and burns with the formation of fumes of P_2O_5 (Lampadius, 1806). A solution in ether shows phosphorescence when poured on hot water or rubbed on the skin.

Place a few bits of phosphorus in water in a test-tube supported in a beaker of water. Heat the water in the beaker and pass a current of oxygen through a tube into the water in the test-tube above the phosphorus. When the temperature reaches 60° the phosphorus takes fire and burns under water in contact with the oxygen, forming flakes of red phosphorus and a solution of phosphoric acid.

Sticks of white phosphorus under water in presence of air slowly acquire a white crust, which is ordinary phosphorus detached by unequal oxidation; according to Baudrimont (1865) it is not formed in water free from air. This crust slowly turns red and the colour spreads through the mass.

White phosphorus is very poisonous, the lethal dose being about 0.15 gm. Workmen exposed to the vapour are liable to decay of the bones, especially of the jaw ("phossy-jaw"), and its use in the manufacture of matches has ceased.

The modern "strike anywhere" matches have heads containing phosphorus sulphide P_4S_3 , oxidising agents such as potassium chlorate or manganese dioxide, glue or gum as a binder, and powdered glass to increase the friction. The heads of safety matches contain no phosphorus but are compounded of antimony sulphide and sulphur and oxidising agents such as potassium chlorate and red lead, whilst the strip on the box contains red phosphorus, powdered glass and a binder.

Besides ordinary or α -white phosphorus a second crystalline form, β -white phosphorus (hexagonal), is known: it is formed when ordinary white phosphorus is cooled to -76.9° or is subjected to about 12,000 atm. pressure.

Red phosphorus was prepared by Schrotter in 1845 by heating white phosphorus for a few hours at 250° in a flask filled with nitrogen or carbon dioxide. The liquid deposits a red powder and finally solidifies

to a purplish-red mass. The transformation begins at about 215° , is fairly rapid at 250° , and at higher temperatures it is reversible and is strongly exothermic: $P(\text{white}) = P(\text{red}) + 4.22 \text{ k. cal.}$ Red phosphorus also remains when white phosphorus burns in air, or in oxygen under water, and was formerly thought to be a suboxide.

Brodie (1853) showed that the transformation is catalysed by a little iodine, and then occurs at 200° . The change occurs when a little iodine or selenium is added to a solution of white phosphorus in carbon disulphide.

Red phosphorus is made by heating about a ton of white phosphorus in a large cast-iron pot with a cover, through which passes an upright iron tube. The pot is uniformly heated at 240° , the temperature being controlled by thermometers protected by iron tubes, since phosphorus attacks glass. A little phosphorus burns, absorbing oxygen from the air in the vessel. The hard solid in the pot is ground under water and boiled with caustic soda solution to remove unchanged white phosphorus. It is repeatedly washed with hot water and dried with steam. It usually contains about 0.5 per cent of white phosphorus and some phosphoric acid.

Commercial red phosphorus is a violet-red powder, density 2.1–2.2 without smell or taste and is not poisonous. It is a feeble conductor of electricity. It melts under pressure at 592.5° , but on heating at atmospheric pressure is converted directly into vapour, which condenses to white phosphorus on cooling.

Heat a little red phosphorus in a hard glass test-tube in a slow current of dry carbon dioxide passed through a tube in a rubber stopper also fitted with an outlet tube. White phosphorus condenses on the upper cool part of the test-tube.

Red phosphorus in general is much less reactive than white phosphorus. It does not glow in air but on exposure becomes moist from slow oxidation to phosphoric acid. It does not ignite in air below 240° , does not burn in chlorine unless heated, burns quietly in contact with liquid bromine, and does not inflame in contact with solid iodine but combines without incandescence on heating. It is insoluble in carbon disulphide and in hot alkali hydroxide solution, but dissolves in concentrated nitric acid, rapidly on heating.

White phosphorus is metastable under all conditions and tends to pass into red, although the change is very slow at the ordinary temperature in the dark. If liquid white phosphorus is contained in one limb of a U-tube at 324° and solid red phosphorus in the other limb at 350° , distillation occurs to the hotter limb.

Ordinary red phosphorus was thought by Schrötter to be amorphous, but it really contains small rhombohedral crystals (Pedler, 1890; Retgers, 1893). The colour varies according to the temperature of preparation, from reddish-yellow through bright sealing-wax red (sp. gr. 2.15), to dark violet-red (sp. gr. 2.34) after long heating. The

colour depends on the particle size and the extent of development of crystalline form. Yellow and scarlet forms are amorphous, and some kinds of commercial red phosphorus are mixtures of the scarlet amorphous and the violet crystalline forms.

Scarlet amorphous phosphorus is obtained as a fine powder by exposing a solution of white phosphorus in carbon disulphide or phosphorus tribromide to sunlight, when the yellow powder first deposited turns red (Pedler), or by boiling a 10 per cent solution of white phosphorus in phosphorus tribromide for ten hours (Schenck). It is a fine scarlet powder, sp. gr. 1.876, more active than common red phosphorus, but oxidising only very slowly in air, and is not poisonous. It dissolves in alkali with evolution of phosphine and turns black. Prepared in this way it contains phosphorus tribromide: it may be obtained pure by heating phosphorus tribromide with mercury at 240° (Wolf, 1915): $2\text{PBr}_3 + 3\text{Hg} \rightarrow 2\text{P} + 3\text{HgBr}_2$.

The *crystalline forms of red phosphorus* are called **Phosphorus-III** and **Phosphorus-IV**.

The common form is **Phosphorus-III** or **violet phosphorus** (also called *α-metallic phosphorus*), discovered by Hittorf in 1865. It is formed by heating ordinary red phosphorus in a sealed tube at 530°, the upper part of the tube being kept at 444°, when it sublimes in brilliant opaque rhombohedral crystals, isomorphous with As, Sb and Bi, sp. gr. 2.316 or 2.34, m.pt. 592.5°. The crystals are also formed by dissolving white phosphorus in fused lead or bismuth in a sealed tube, allowing to crystallise, and dissolving out the metal in dilute nitric acid or electrolytically (Stock and Gomolka, 1909). It does not oxidise in air and is a non-conductor of electricity. It is probably the same as the **violet phosphorus**, sp. gr. 2.35, m. pt. 589.5°, obtained by Bridgman (1916) by heating white phosphorus with a trace of sodium under very high pressure.

Phosphorus-IV or **black phosphorus** (or *β-metallic phosphorus*), discovered by Bridgman (1914), is crystalline, sp. gr. 2.69, m. pt. 587.5°, and is formed irreversibly from white phosphorus at 200° under a pressure of 12,000 kg./sq. cm. It does not ignite at 400° in air and is a fairly good conductor of electricity.

A provisional *phase diagram* for phosphorus is shown in Fig. 294, but the actual relations are rather complicated. The curves and transition points are similar to those for the sulphur system (p. 452).

AB is the vapour pressure curve of solid violet phosphorus (P-III), lying below the curves of the metastable forms. *FE* is the curve of solid white phosphorus (P-I) and *EX* that of the liquid, probably continuous with the vapour pressure curve *BY* of liquid violet phosphorus. *BD* represents the equilibrium between violet phosphorus and liquid and the transition point

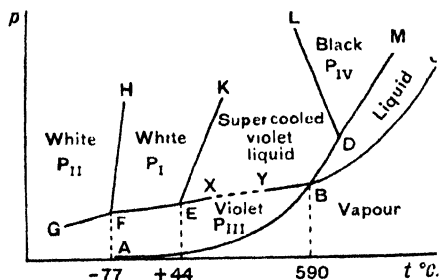


FIG. 294.—Phase diagram of phosphorus.

D to black phosphorus (P-IV) is a triple point (P-III, P-IV, liquid). *DL* gives the variation of the transition temperature of violet to black with change of pressure. *C* is the critical point of liquid phosphorus, about 695° and 82 atm. The values of dT/dp along *FH* (P-II \rightleftharpoons P-I) and *EK* (P-I \rightleftharpoons liq.) are 0.012° and 0.029° per atm., respectively.

The glow of phosphorus.—The vapour pressure of white phosphorus at 20° is 0.027 mm. and the vapour oxidises spontaneously in air, emitting a faint green glow and white fumes. The glow is produced with mere traces of phosphorus vapour (5×10^{-5} per cent in a gas in the absence of inhibitors), and is used as a test for free white phosphorus (*Mitscherlich's test*).

A piece of white phosphorus is boiled in water in a flask connected with a Liebig's condenser. Phosphorus distils with the steam and a glow is seen in a dark room at the place where the vapour and steam condense in the tube.

In Smithells' *cold flame* experiment, a few pieces of dry white phosphorus are placed in a dry bolt-headed and covered with dry glass wool, the flask is heated on a water-bath, and a stream of dry carbon dioxide passed through (Fig. 295). The phosphorus vapour oxidises in the air and a green flame is seen in a dark room at the top of the exit tube. This is so cool that a finger may be held in it, and it will not kindle a match.

The glow of phosphorus was first investigated by Boyle (1680-82), who discovered most of its main features :

- (i) Phosphorus glows only in presence of air.
- (ii) An acid is formed which differs from phosphoric acid in giving little flashes of light on heating [phosphine from phosphorous acid].
- (iii) The glow is produced by very small quantities of phosphorus (1 part in 500,000 parts of water).
- (iv) The glow is produced by solutions of phosphorus in olive oil and some other oils, but oils of mace and aniseed prevent it.
- (v) After long exposure to phosphorus, air acquires a strong odour [ozone] distinct from the visible fumes.

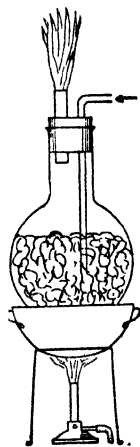


FIG. 295.—The cold flame experiment.

About the same time, Lemery, Slarc and Hauksbee found that the glow is brighter at lower air pressures. Lampadius showed that it is extinguished in a Torricellian vacuum (the space in a barometer tube), so that a trace of oxygen is necessary. Fourcroy (1788) found that phosphorus does not glow in ordinary moist oxygen at atmospheric pressure, but Bellani de Monza (1813) showed that the glow appears if the oxygen pressure is reduced, an observation confirmed by Schweigger (1824) and Graham (1829).

According to Russell (1903), phosphorus glows very feebly at atmospheric pressure in oxygen dried by sulphuric acid, or even at higher pressures if the surface is very clean, lower oxides of phosphorus being produced. At pressures lower than 500 mm. at room temperature the glow in dry oxygen becomes much brighter, and phosphorus pentoxide is formed. Ozone is not formed in dry oxygen. The main product of the glow in air at ordinary temperature is phosphorus dioxide P_2O_4 (not P_2O_3), with some P_2O_5 (Miller, 1929). According to Dixon and Baker (1889) phosphorus does not glow at any pressure in oxygen dried by phosphorus pentoxide.

The glow appears in ordinary oxygen if this is mixed with an inert gas, and phosphorus glows in ozonised oxygen at atmospheric pressure. In oxygen at atmospheric pressure the glow appears at 27° and is very bright at 36° , when the phosphorus very easily inflames.

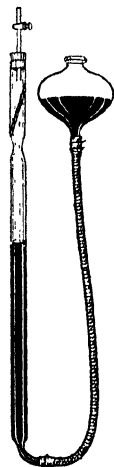


FIG. 296.—Effect of pressure on the glow of phosphorus.

A stick of phosphorus is placed in the constricted part of a tube containing oxygen confined over mercury, the levelling tube being adjusted so that the gas is at atmospheric pressure (Fig. 296). No glow is seen in the dark. If the levelling tube is lowered so as to reduce the pressure, the phosphorus begins to glow.

Heat a piece of phosphorus with olive oil in a flask on a water-bath. Cool the solution and pour it into a round litre flask fitted with a rubber stopper with two delivery tubes. Displace the air by dry oxygen. The glow ceases. Close one tube with rubber tubing and a clip and connect the other with an air-pump. Shake the liquid round the inside of the flask. On reducing the pressure of the oxygen the glow appears suddenly at a certain reduced pressure.

Graham (1829) found that the glow is inhibited by the vapours of ether, naphtha, and turpentine. (The action of essential oils had been observed by Boyle.) One part of turpentine vapour in 4444 parts of air was sufficient. Later observers found that the vapours of many essential oils, camphor, naphthalene, carbon disulphide, and especially iodobenzene, inhibit the glow.

Schönbein (1848) related the glow to the formation of ozone, since (1) essential oils which destroy or dissolve ozone inhibit the luminosity, (2) at low temperatures no ozone is formed and phosphorus does not glow, (3) at 25° the glow is brightest and the production of ozone is a maximum. It is doubtful if ozone is directly formed by the glow reaction, and Downey reported that ozone is formed by the action of the ultra-violet light of the

glow on oxygen, being formed when this light is passed into oxygen through a quartz or fluorite window, but Busse (1927) and Fischbeck and Eich (1938) could not confirm this.

An old theory that the glow was due to the oxidation of P_2O_3 first formed was disproved by Miller (1926), who showed that carefully purified P_2O_3 , freed from white phosphorus by recrystallisation from CS_2 , exposure to light, and sublimation, does not glow in air and also inhibits the glow of phosphorus.

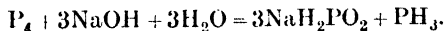
The glow reaction occurs between phosphorus vapour and oxygen, since it is brighter at lower pressures, and an indifferent gas (N_2 or H_2) when passed over phosphorus glows when mixed with oxygen. In a stream of air the glow is detached from the solid phosphorus. There is also a lower limit of oxygen pressure below which phosphorus does not glow. The glow seems to be the result of a chain reaction (p. 216), involving the production of lower oxides of phosphorus, taking place between P_4 and O_2 molecules.

PHOSPHORUS HYDRIDES

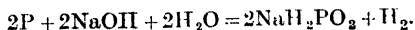
Two well-defined phosphorus hydrides are known, the gaseous phosphorus trihydride PH_3 (*phosphine* or *phosphoretted hydrogen*) and the liquid phosphorus dihydride P_2H_4 . Some ill-defined solid hydrides ($P_{12}H_6$, P_5H_2 and P_9H_2) are probably impure red phosphorus.

Phosphine PH_3 was discovered by Gengembre (1783) by heating white phosphorus with alkali (see below). Traces are formed by heating white or red phosphorus in hydrogen, or by adding bits of white phosphorus to a mixture of zinc and dilute sulphuric acid evolving hydrogen, which then burns with a green flame (this is a sensitive test for free white phosphorus). It is formed by the putrefaction of proteins (Gautier and Étard 1882), and the bacterial reduction of phosphates in the soil (Rudakov, 1927), and its spontaneous inflammability has been invoked to explain the *Will-o'-the-wisp* seen in marshes.

Phosphine is usually prepared by heating white phosphorus with concentrated sodium or potassium hydroxide solution, or a paste of slaked lime, when a hypophosphite is also formed :



Some hypophosphite is decomposed, so that 60 per cent of hydrogen may be present in the gas : $NaH_2PO_2 + 2NaOH = 2H_2 + Na_3PO_4$; baryta gives a purer gas. Hydrogen is also evolved by the direct reaction :



Pure phosphine may be obtained by absorbing it from the gas in a solution of cuprous chloride in hydrochloric acid (when $CuCl, PH_3$ is formed), heating the solution, and drying the gas with KOH and P_2O_5 (Riban, 1879).

A few pieces of white phosphorus are placed in a flask (Fig. 297) containing 30–40 per cent sodium hydroxide solution. The air is displaced by coal

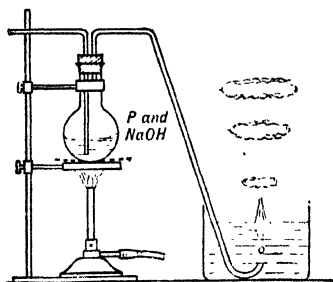
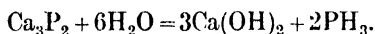


FIG. 297. - Preparation of phosphine.

gas to avoid explosion, and the flask heated to a fairly high temperature. Each bubble of phosphine which escapes from the delivery tube dipping into water ignites spontaneously with a bright flash, and a vortex-ring of white smoke (particles of metaphosphoric acid) rises in still air.

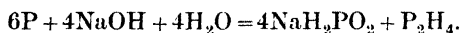
Spontaneously inflammable phosphine is formed by the action of water on crude calcium phosphide :



A few pieces of calcium phosphide are dropped into a beaker of water and covered with an inverted funnel immersed in the water. The bubbles of gas inflame spontaneously in air.

A purer gas is formed by the action of dilute hydrochloric acid on calcium phosphide. The gas from *pure* calcium phosphide is not spontaneously inflammable (Moissan, 1899).

The spontaneous inflammability of ordinary phosphine is, as Le Verrier (1835) suspected and Thenard (1844) proved, due to a small amount of the vapour of phosphorus dihydride also formed :

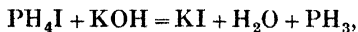


Thenard passed the gas through a tube immersed in a freezing mixture, when the liquid hydride deposits and the gas is no longer spontaneously inflammable. The same result is obtained by passing the gas over recently ignited charcoal, which adsorbs the vapour of the dihydride, or by mixing the gas with a little ether vapour. The pure gas becomes spontaneously inflammable if mixed with a little vapour of fuming nitric acid.

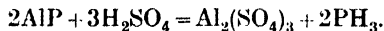
Phosphine which is not spontaneously inflammable, but may contain 6 per cent of hydrogen, is evolved on heating phosphorous acid (Davy, 1812) :



Pure phosphine is prepared by dropping 30 per cent potassium hydroxide solution on phosphonium iodide mixed with broken glass :



washing with hydrochloric acid (to decompose P_2H_4) and sodium hydroxide (to remove HI) and drying with P_2O_5 ; or by the action of dilute sulphuric acid on aluminium phosphide (prepared by heating aluminium powder and red phosphorus) :

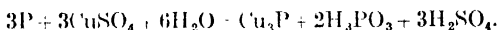


Phosphine is a colourless gas with a very unpleasant smell of rotten fish

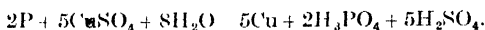
and is poisonous; normal density 1.5307 gm./lit., m. pt. -132.5° , b. pt. -87.4° . It is sparingly soluble in water (0.26 vols. in 1 of water at 17°), alcohol and ether: a crystalline *hydrate* ($\text{PH}_3 \cdot \text{H}_2\text{O}$ or PH_4OH ?) is formed by releasing the pressure on a mixture of the liquid and water. The gas is decomposed at 440° by a first order reaction largely on the surface of the vessel (Hinshelwood and Topley, 1924), and by electric sparks, 2 vols. depositing red phosphorus and giving 3 vols. of hydrogen: $2\text{P}_x\text{H}_y = 2x\text{P} + 3\text{H}_2$, $\therefore y=3$ and the formula is P_xH_3 . The density shows that the mol. wt. is 34, \therefore the molecule contains $34 - 3 = 31$ parts of phosphorus, or 1 at. wt., hence $x=1$ and the formula is PH_3 . When passed over heated copper, phosphine forms copper phosphide and hydrogen.

Phosphine inflames in air at about 150° . When burnt in a test-tube it deposits phosphorus (cf. H_2S , p. 457). A mixture of pure phosphine with air or oxygen explodes when the pressure is reduced (Labillardière, 1817): very pure and dry phosphine explodes with oxygen at all pressures, traces of moisture lowering the inflammation pressure (Trautz and Gabler, 1929). Mixtures with nitric and nitrous oxides explode when sparked: $\text{PH}_3 + 4\text{N}_2\text{O} = \text{H}_3\text{PO}_4 + 4\text{N}_2$. Phosphine ignites spontaneously in chlorine: $\text{PH}_3 + 4\text{Cl}_2 = \text{PCl}_5 + 3\text{HCl}$. It combines with many metallic chlorides. The pure gas is completely absorbed by a solution of bleaching powder. It precipitates phosphides or metals from solutions of many metallic salts (e.g. CuSO_4 , AgNO_3). These phosphides are also formed by heating the solutions with white phosphorus, or the metals with phosphorus, or the phosphates with carbon in the electric furnace.

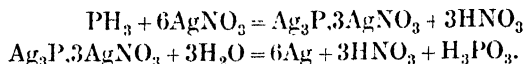
Heat a few pieces of white phosphorus with a solution of copper sulphate. Black copper phosphide Cu_3P is formed:



In the cold, metallic copper is slowly deposited:



From silver nitrate solution, phosphine precipitates silver, a yellow intermediate compound being formed (cf. AsH_3 , p. 457):



Phosphonium compounds.—Although phosphine is neutral it can act as a feeble base, forming phosphonium salts PH_4X analogous to ammonium salts NH_4X . A mixture of phosphine and dry hydrogen chloride does not react at atmospheric pressure, but if cooled to -35° or compressed to 18 atm. at 15° , it deposits white cubic crystals of phosphonium chloride which dissociate again on warming or on reducing the pressure:

$\text{PH}_3 + \text{HCl} \rightleftharpoons \text{PH}_4\text{Cl}$. **Phosphonium bromide** PH_4Br is more stable and is produced in cubic crystals when a mixture of PH_3 and HBr gas is led into a moderately cooled flask, or phosphine is passed into cold saturated hydrobromic acid (Ogier, 1879). **Phosphonium iodide** PH_4I (Davy, 1812) is fairly stable and is formed in white tetragonal crystals on mixing PH_3 and HI gas at the ordinary temperature and pressure. It dissociates at 30° but the crystals can be sublimed. It is prepared by the following process.

10 gm. of white phosphorus are dissolved in an equal weight of carbon disulphide in a tubulated retort, from which the air has been removed by a current of dry carbon dioxide : 17 gm. of iodine are then added and the carbon disulphide is distilled off completely on a water-bath in a current of CO_2 . After cooling, the neck of the retort is connected with a wide glass tube

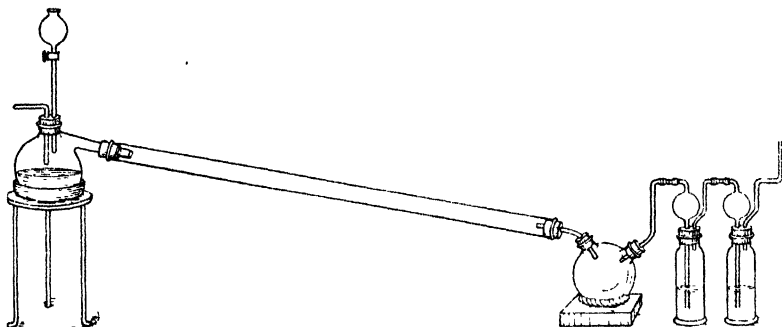


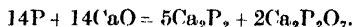
FIG. 298.— Preparation of phosphonium iodide.

and receiver and 8.5 ml. of water are dropped gradually on to the phosphorus iodide (Fig. 298). The retort is then heated, at first gently, later more strongly to sublime the PH_4I into the tube. Two wash-bottles containing water are attached to the receiver, to absorb the hydriodic acid evolved : $2\text{P} + \text{I}_2 + 4\text{H}_2\text{O} = \text{PH}_4\text{I} + \text{H}_3\text{PO}_4 + \text{HI}$.

Phosphorus dihydride P_2H_4 is condensed as a colourless liquid from crude phosphine by passing through a tube cooled in a freezing mixture.

The phosphine formed by the action of water on crude calcium phosphide, perhaps containing Ca_2P_2 ($\text{Ca}-\text{P}-\text{P}-\text{Ca}$), is fairly rich in P_2H_4 vapour : $\text{Ca}_2\text{P}_2 + 4\text{H}_2\text{O} = 2\text{Ca}(\text{OH})_2 + \text{P}_2\text{H}_4$.

The calcium phosphide is a reddish-brown solid prepared by passing phosphorus vapour over quicklime heated to dull redness :



It is used for making *Holmes's signal* for use at sea. This is a sealed tin canister filled with calcium phosphide and attached to a wooden float. The canister is pierced above and below and thrown overboard. The gas ignites spontaneously and burns with a luminous flame.

In the preparation of the liquid hydride pieces of calcium phosphide are dropped through a wide tube into water at 60° in a Woulfe's bottle (Fig. 299), the air being previously displaced by hydrogen. The gas is passed through a tube cooled in water to deposit moisture and the liquid condensed in a Hofmann tube cooled in a freezing mixture.

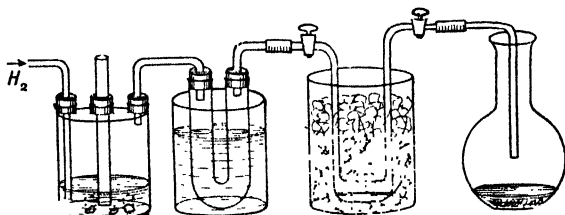


FIG. 299. Preparation of liquid phosphorus hydride.

The formula P_2H_4 , analogous to that of hydrazine, is confirmed by the vapour density below atmospheric pressure (mol. wt. 66.15). The b.pt. (extrapolated) is $+51.7^\circ/760$ mm., the m.pt. -99° . The vapour is unstable and the liquid also decomposes on exposure to light, evolving phosphine and depositing a yellow solid formerly regarded as a solid hydride $P_{12}H_6$, but probably impure amorphous phosphorus (Royen and Hill, 1936): $3P_2H_4 = 2P + 4PH_3$.

The same solid is formed if the uncondensed vapours from the preparation are passed into a flask containing a little fuming hydrochloric acid. Another solid hydride P_9H_2 was said to be formed by heating $P_{12}H_6$ in vacuum: $5P_{12}H_6 \cdot 6P_9H_2 + 6PH_3$, and another, P_5H_2 , by the action of very dilute acetic acid on Na_2P_5 .

PHOSPHORUS HALIDES

Phosphorus combines with halogens to form two series of compounds in which it is 3- and 5-valent, PX_3 or PX_5 , being formed according as phosphorus or halogen is in excess. Iodine forms PI_3 and P_2I_4 , the existence of PI_5 being doubtful, and there is a chloride P_2Cl_4 . The physical properties of the halides are:

PF_3 colourless gas, b.pt. -95° , m.pt. -160° .

PF_5 colourless gas, b.pt. -84.5° , m.pt. -93.7° .

P_2Cl_4 colourless liquid, b.pt. 180° , m.pt. -28° .

PCl_3 colourless liquid, b.pt. 76° , m.pt. -112° , sp. gr. 1.613 at 0° .

PCl_5 white tetragonal crystals, sublimes at 162.8° , m.pt. 166.8° under pressure.

PBr_3 colourless liquid, b.pt. 172.9° , m.pt. -40° , sp. gr. 2.885 at 0° .

PBr_5 yellow rhombic crystals, b.pt. 106° , decomposes on heating.

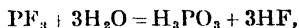
P_2I_4 orange red triclinic crystals, m.pt. 124.5° .

PI_3 dark red hexagonal crystals, m.pt. 61° , b.pt. 120° at 15 mm.

Some mixed halides, e.g. PCl_4Br and PF_3Cl_2 are known.

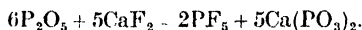
Phosphorus trifluoride PF_3 (Moissan, 1884) is formed by the action of arsenic trifluoride on phosphorus trichloride: $PCl_3 + AsF_3 = PF_3 + AsCl_3$;

by warming phosphorus tribromide with zinc fluoride: $2\text{PBr}_3 + 3\text{ZnF}_2 = 2\text{PF}_3 + 3\text{ZnBr}_2$; and by heating copper phosphide with lead fluoride. The gas does not fume in air and has no action on glass in the cold; it is hydrolysed by water:



and is decomposed by sparking: $5\text{PF}_3 = 3\text{PF}_5 + 2\text{P}$. A mixture of the vapour with oxygen explodes when sparked, phosphorus oxyfluoride POF_3 being formed.

Phosphorus pentafluoride PF_5 (Thorpe, 1877) is formed when phosphorus burns in fluorine; when arsenic trifluoride is mixed with phosphorus pentachloride in a freezing mixture: $3\text{PCl}_5 + 5\text{AsF}_3 = 3\text{PF}_5 + 5\text{AsCl}_3$; by warming phosphorus fluobromide (made by cooling a mixture of bromine and PF_3 to -20°) at 15° : $5\text{PF}_3\text{Br}_2 = 3\text{PF}_5 + 2\text{PBr}_5$; and by heating a mixture of 25 gm. of phosphorus pentoxide and 55 gm. of powdered fluorspar in an iron tube:

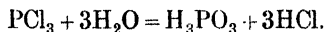


The gas has the normal density corresponding with PF_5 , does not attack glass when dry, fumes in air: $\text{PF}_5 + \text{H}_2\text{O} = \text{POF}_3 + 2\text{HF}$, and combines with ammonia gas to form solid $2\text{PF}_5 \cdot 5\text{NH}_3$.

Phosphorus oxyfluoride POF_3 is obtained by heating a mixture of powdered cryolite and phosphorus pentoxide in a brass tube; it is a colourless gas, b.pt. -39.8° , m.pt. -68° , which may be collected over mercury. It is also formed by the action of dry hydrogen fluoride on phosphorus pentoxide, and of zinc fluoride on phosphorus oxychloride.

Phosphorus dichloride P_2Cl_4 is an oily fuming liquid formed by the action of a silent discharge on a mixture of PCl_3 vapour and hydrogen, and by the action of a zinc arc on PCl_3 (Stock, 1925). It is probably $\text{Cl}_2=\text{P}-\text{P}=\text{Cl}_2$.

Phosphorus trichloride PCl_3 is a colourless liquid made by passing a stream of dry chlorine over white or red phosphorus in a retort, and condensing in a cooled dry receiver (Gay-Lussac and Thenard, 1808). It is purified by standing over white phosphorus (which removes excess of chlorine) and redistilling, and may be kept in sealed tubes. The vapour density is normal. The liquid fumes strongly in moist air and reacts violently with water, forming phosphorous acid:



It forms $\text{PCl}_3 \cdot 6\text{NH}_3$ and $\text{PCl}_3 \cdot 8\text{NH}_3$ with ammonia, and reacts violently with sulphur trioxide: $\text{PCl}_3 + \text{SO}_3 = \text{POCl}_3 + \text{SO}_2$. It is decomposed by hot concentrated sulphuric acid: $\text{PCl}_3 + 2\text{H}_2\text{SO}_4 = \text{SO}_3\text{HCl} + \text{SO}_2 + 2\text{HCl} + \text{HPO}_3$, by sulphur chloride: $3\text{PCl}_3 + \text{S}_2\text{Cl}_2 = \text{PCl}_5 + 2\text{PSCl}_3$, and by liquid hydrogen sulphide (forming phosphorus sulphide).

31 gm. of white phosphorus is cut under water into pieces. These are dried between filter paper one at a time and inserted by crucible tongs into a dry tubulated retort previously filled with carbon dioxide. A good cork carrying a lead-in tube which can be moved is fitted to the tubulure of the retort,

and the tube attached by rubber tubing to the drying tube of a chlorine apparatus (Fig. 300). The retort is connected with a cooled dry receiver with a calcium chloride tube attached. Chlorine is passed in, the retort not

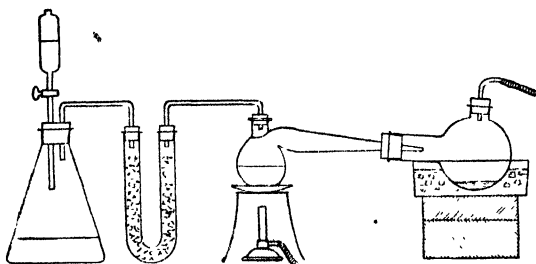


FIG. 300.—Preparation of phosphorus trichloride.

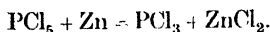
being heated. The phosphorus burns with a pale flame forming PCl_3 , which distills over. The stream of chlorine must pass rapidly and steadily; if a white sublimate (PCl_5) forms, lower the inlet tube nearer the phosphorus; if a yellowish-red sublimate forms, raise the tube.

Phosphorus pentachloride PCl_5 (Davy, 1810; Dulong, 1816) is a white or pale greenish-yellow solid formed by burning phosphorus in excess of chlorine or by dropping phosphorus trichloride into dry chlorine: $\text{PCl}_3 + \text{Cl}_2 = \text{PCl}_5$.

Allow PCl_3 to drop slowly into a dry flask cooled in ice, through which a stream of dry chlorine is passed. A white powder of PCl_5 collects in the flask (Fig. 301).

Phosphorus pentachloride sublimes without previous fusion when heated below 100° at ordinary pressure. The vapour is dissociated, completely above 300° : $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$. The solid melts under pressure when heated in a sealed tube. When volatilised in an atmosphere of PCl_3 vapour the dissociation is repressed (by mass action) and the normal density of PCl_5 is found. This is found by volatilising PCl_5 and PCl_3 in a Dumas bulb, weighing the mixed vapour, and then analysing the contents of the bulb (Wurtz, 1873).

In PCl_5 two atoms of chlorine are very reactive and many metals (zinc, cadmium, and even gold and platinum) are converted into chlorides when heated with it:



In the vapour state the molecules PF_5 , PCl_5 and PCl_3F_2 are trigonal bipyramids with the phosphorus atom at the centre (Brockway and Beach, 1938). In solid PCl_5 crystals the tetrahedral ions PCl_4^+ and the octahedral

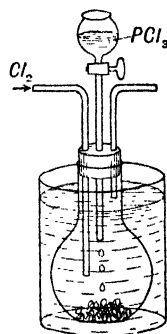
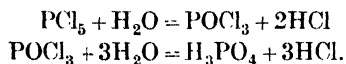


FIG. 301.—Preparation of phosphorus pentachloride.

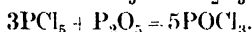
ions PCl_6^- are arranged in a tetragonal lattice which may be regarded as a distorted CsCl lattice. In solid PBr_5 the ions are PBr_4^+ and Br^- (Clark, Powell and Wells, 1942).

Phosphorus pentachloride is violently and irreversibly hydrolysed by water. The reaction may proceed in two stages. With a little water, liquid *phosphorus oxychloride* (or phosphoryl chloride) POCl_3 is formed (Wurtz, 1847), which is hydrolysed by excess of water to *orthophosphoric acid* (of which it is the acid chloride) :



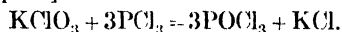
Phosphorus oxychloride is a colourless fuming liquid, b.pt. $107\cdot2^\circ$, m.pt. $1\cdot38^\circ$, sp. gr. 1.712 at 0° , formed by the action of a little water on phosphorus pentachloride, and by many other reactions :

(i) By heating a mixture of PCl_5 and P_2O_5 in a sealed tube :

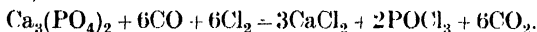


(ii) By oxidising PCl_3 with ozone : $\text{PCl}_3 + \text{O}_3 = \text{POCl}_3 + \text{O}_2$.

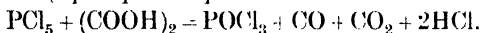
(iii) By *gradually* adding 32 gm. of powdered potassium chlorate to 100 gm. of phosphorus trichloride and distilling (Dervin, 1883) :



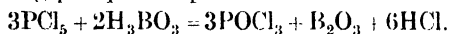
(iv) By heating a mixture of calcium phosphate and carbon at 300° – 350° in a mixture of chlorine and carbon monoxide (Riban, 1882) :



(v) By distilling phosphorus pentachloride with oxalic acid :



(vi) By distilling phosphorus pentachloride with boric acid :



Phosphorus oxychloride sinks in water and *slowly* dissolves, being hydrolysed : $\text{POCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 3\text{HCl}$. With water and excess of zinc dust it evolves phosphine (PCl_3 does not).

Phosphorus bromides and iodides.—White phosphorus explodes in contact with liquid chlorine or bromine : liquid bromine dropped on red phosphorus in a cooled flask reacts with evolution of light and **phosphorus tribromide** PBr_3 distils. By adding bromine to this, yellow solid **phosphorus pentabromide** PBr_5 is formed. The vapour is dissociated : $\text{PBr}_5 \rightleftharpoons \text{PBr}_3 + \text{Br}_2$. **Phosphorus oxybromide** POBr_3 is a colourless crystalline solid, m.pt. 56° , b.pt. 198° , formed by the action of a little water or of oxalic acid on PBr_5 : it is formed by oxidising PBr_3 .

White phosphorus inflames in contact with iodine ; **phosphorus di-iodide** P_2I_4 and **phosphorus tri-iodide** PI_3 are formed by mixing solutions of iodine and white phosphorus in carbon disulphide in the correct ratios and evaporating. PI_5 and POI_3 are not definitely known. The di-iodide is probably $\text{I}_2\text{P}\cdot\text{PI}_2$.

OXIDES AND OXYACIDS OF PHOSPHORUS

Phosphorus trioxide	P_2O_3 or P_4O_6	Hypophosphorous acid	H_3PO_2
Phosphorus tetroxide	P_2O_4 or P_8O_{16}	Phosphorous acid	H_3PO_3
Phosphorus pentoxide	P_2O_5 or P_4O_{10}	Hypophosphoric acid	$H_4P_2O_6$
		Phosphoric acids :	
		orthophosphoric acid	H_3PO_4
		pyrophosphoric acid	$H_4P_2O_7$
		metaphosphoric acid	HPO_3

The so-called **phosphorus suboxides** P_4O and P_2O are impure red phosphorus. A violet solid said to contain a soluble phosphorus peroxide PO_3 is formed by the action of an electric discharge on a mixture of P_2O_5 vapour and oxygen (Schenk and Platz, 1936). Two **perphosphoric acids** H_3PO_5 and $H_4P_2O_8$ and salts are known.

White phosphorus burns in a free supply of air to form **phosphorus pentoxide**, first observed by Boyle and called "flowers of phosphorus". In a limited supply of air some phosphorus trioxide is formed. The phosphorus is extinguished before all the oxygen is removed, and part is converted into red phosphorus.

Dry the air inside a tall bell-jar by a capsule of sulphuric acid. After a few hours remove the capsule and replace it by a porcelain crucible supported on a cork, in which a bit of phosphorus is placed. The phosphorus is ignited by touching with a hot wire. Notice the bright flame and the formation of a snow-white powder (P_2O_5) which rapidly settles. After a time the flame becomes larger, greenish and flickering and P_2O_3 is formed. Red phosphorus remains.

Phosphorus pentoxide is prepared by the combustion of phosphorus in air or oxygen and is very stable even at high temperature (cf. N_2O_5 and As_2O_5).

The apparatus shown in Fig. 302 is used. The sheet-iron cylinder has an opening at the side through which a copper spoon containing burning phosphorus is introduced. The pentoxide settles into the dry bottle below. Several portions of phosphorus are burnt. Air enters between the iron funnel h and the cylinder on removing i .

Commercial phosphorus pentoxide contains some trioxide and metaphosphoric acid. It is purified by volatilising in a current of dry air or oxygen in a hard glass or iron tube, and condensing in a cooled receiver. Lower oxides of phosphorus are oxidised to P_2O_5 by heating at 175° - 220° in a current of ozonised air. The purified product, if free from lower oxides, should give no black colour with silver nitrate solution.

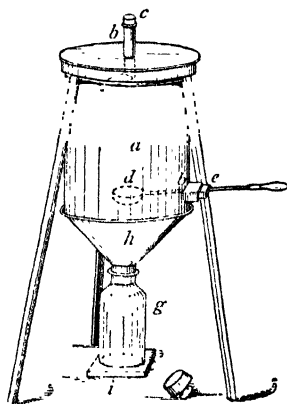


FIG. 302. --Preparation of phosphorus pentoxide.

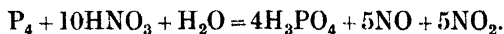
The white voluminous powder of phosphorus pentoxide becomes more compact and less volatile at 440°. If distilled in dry carbon dioxide it forms hexagonal crystals subliming at 250°. There are also rhombic and tetragonal forms. The compact variety melts under pressure at 565°, forming a vitreous mass. The vapour density at 1400° is a little higher than corresponds with P_4O_{10} (for the structure see p. 586).

Phosphorus pentoxide shows strong phosphorescence after illumination, especially at low temperatures. It has a powerful affinity for water, becoming moist and sticky on exposure to air from formation of metaphosphoric acid, and it withdraws the last traces of moisture from gases. When thrown into water it reacts with a hissing noise and flocks of metaphosphoric acid separate: $P_2O_5 + H_2O = 2HPO_3$. On standing in the cold these slowly dissolve: the metaphosphoric acid hydrates to pyrophosphoric acid and this slowly to orthophosphoric acid; the changes occur rapidly on boiling (Holt and Myers, 1911). Phosphorus pentoxide withdraws the elements of water from oxyacids, forming the acid anhydrides, e.g. SO_3 from H_2SO_4 , N_2O_5 from HNO_3 , and Cl_2O_7 from $HClO_4$.

Orthophosphoric acid.—The natural mineral phosphates and bone-ash contain salts of orthophosphoric acid H_3PO_4 , and the fertiliser *guano* (excreta of sea-birds) is rich in phosphates and combined nitrogen. Another source of fertiliser phosphate is the *basic slag* of steel furnaces, containing $Ca_4P_2O_9$ or $Ca_3(PO_4)_2 \cdot CaO$. The acid was prepared by Marggraf in 1743 from phosphorus by combustion. He also noticed that phosphorus increases in weight on combustion. Scheele obtained the acid by oxidising phosphorus with nitric acid.

Commercial orthophosphoric acid is prepared by digesting bone-ash with diluted sulphuric acid, sp. gr. 1.5, for several hours: $Ca_3(PO_4)_2 + 3H_2SO_4 + 3CaSO_4 + 2H_3PO_4$. The calcium sulphate is filtered off and the phosphoric acid evaporated to sp. gr. 1.7 (85 per cent H_3PO_4). The product is impure, and contains acid calcium phosphate $CaH_4(PO_4)_2$. Phosphoric acid is also made by a furnace process (p. 564), air being admitted to burn the phosphorus vapour to P_2O_5 , and CO to CO_2 ; water is sprayed into the cooled gas and crude 85 per cent phosphoric acid is separated by electrostatic precipitation. The process may be carried out in a blast furnace (Curtis, 1935–8).

Pure orthophosphoric acid is obtained from phosphorus pentoxide and water, or by oxidising phosphorus with nitric acid:



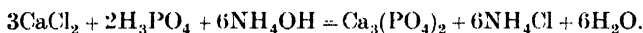
Place 112 ml. of concentrated nitric acid and 183 ml. of water in a 2-litre R.B. flask with a boiling tube, through which cold water is passed, hanging in the neck to serve as a reflux condenser. Add 31 g. of red phosphorus in portions of one-fifth at a time, warming till red vapours appear and cooling

if the reaction is too violent. When all the phosphorus is dissolved (neglect any black residue), add 20 ml. of concentrated nitric acid and heat in a porcelain dish to oxidise phosphorous acid. When reaction ceases and a little of the diluted liquid gives no black precipitate with AgNO_3 (due to H_3PO_3) add an equal volume of water and filter if necessary. Evaporate in a porcelain dish over a small flame till a thermometer in the liquid rises just to 180° . Cool in a vacuum desiccator over concentrated sulphuric acid, placing the desiccator in a freezing mixture of ice and salt in a sink. Deliquescent crystals of orthophosphoric acid slowly deposit. If the temperature is carried beyond 180° in the evaporation some metaphosphoric acid is formed, and crystallisation will not occur.

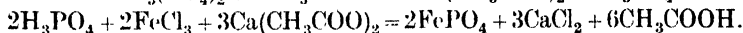
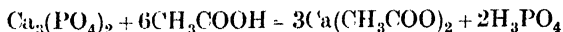
The rhombic crystals of orthophosphoric acid melt at 38.6° or 42.3° and are very soluble in water. Orthophosphoric acid is *tribasic* and forms three series of salts :

primary, e.g. KH_2PO_4 ; *secondary*, e.g. Na_2HPO_4 ; *tertiary*, e.g. Na_3PO_4 .

Ortho-phosphates are usually called simply " phosphates." Ordinary sodium phosphate is the *secondary* salt, $\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$; ordinary potassium phosphate is the *primary* salt KH_2PO_4 ; tertiary sodium phosphate is $\text{Na}_3\text{PO}_4, 12\text{H}_2\text{O}$. The alkali phosphates (except lithium phosphate Li_3PO_4) are soluble in water. The tertiary phosphates of the remaining metals are insoluble in water but dissolve in dilute mineral acids : $\text{Ca}_3(\text{PO}_4)_2 + 6\text{HCl} = 3\text{CaCl}_2 + 2\text{H}_3\text{PO}_4$. They are reprecipitated by adding ammonia :

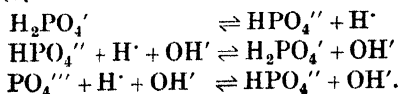


Aluminium phosphate AlPO_4 and ferric phosphate FePO_4 are insoluble in acetic acid, chromium phosphate CrPO_4 is sparingly soluble, but the remaining phosphates are soluble. On adding ferric chloride solution to a solution of a phosphate in acetic acid, the phosphoric acid is precipitated as ferric phosphate and is so removed from the solution :



Excess of ferric chloride forms a red solution of ferric acetate $\text{Fe}(\text{CH}_3\text{COO})_3$, but on boiling this is precipitated as basic ferric acetate, and the filtrate contains the other metals (except aluminium and chromium) which were precipitated as phosphates. These reactions are used in qualitative analysis for the separation of the phosphate radical from a solution.

The alkali primary phosphates are acid to litmus, the secondary phosphates faintly alkaline (practically neutral), and the tertiary phosphates strongly alkaline :



On titration with alkali with litmus as indicator, phosphoric acid behaves as dibasic; methyl orange changes colour at the stage NaH_2PO_4 , and phenolphthalein at the stage Na_2HPO_4 (see Fig. 171); the changes are sharp at 55° . The dissociation constants of ortho-phosphoric acid at 25° are:

$$K_1 = [\text{H}^+][\text{H}_2\text{PO}_4^-]/[\text{H}_3\text{PO}_4] = 7.5 \times 10^{-3}$$

$$K_2 = [\text{H}^+][\text{HPO}_4^{2-}]/[\text{H}_2\text{PO}_4^-] = 6.2 \times 10^{-8}$$

$$K_3 = [\text{H}^+][\text{PO}_4^{3-}]/[\text{HPO}_4^{2-}] = 1.1 \times 10^{-12}$$

Solutions of *ortho*-phosphates with excess of nitric acid and ammonium molybdate solution slowly deposit *in the cold* a canary-yellow precipitate of ammonium phosphomolybdate (p. 893), readily soluble in ammonia.

Pyro- and meta-phosphates do not give this reaction unless heated, or allowed to stand for a long time, when they are converted into orthophosphoric acid. Arsenic acid gives a similar precipitate but *only on heating*. The precipitation of orthophosphoric acid occurs much more rapidly at 60° – 65° .

Magnesia mixture (a solution containing magnesium chloride, ammonium chloride and ammonia) gives with orthophosphates a white crystalline precipitate of magnesium ammonium phosphate $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. Orthophosphates give a yellow precipitate of silver phosphate Ag_3PO_4 with silver nitrate solution, but no precipitate with barium chloride, unless the solution is alkaline.

Pyrophosphoric acid is slowly formed (with a little metaphosphoric acid) when orthophosphoric acid is heated at 213° (rapidly above 240°):



If ordinary sodium phosphate is heated above 240° it loses water and forms sodium pyrophosphate (Clark, 1827): $2\text{Na}_2\text{HPO}_4 = \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$.

Lead nitrate solution and sodium pyrophosphate solution give a white precipitate of lead pyrophosphate $\text{Pb}_2\text{P}_2\text{O}_7$, and with hydrogen sulphide solution this gives a solution of pyrophosphoric acid: $\text{Pb}_2\text{P}_2\text{O}_7 + 2\text{H}_2\text{S} = \text{H}_4\text{P}_2\text{O}_7 + 2\text{PbS}$. Pure pyrophosphoric acid is best prepared by gently heating a mixture of orthophosphoric acid crystals and phosphorus oxychloride: $5\text{H}_3\text{PO}_4 + \text{POCl}_3 = 3\text{H}_4\text{P}_2\text{O}_7 + 3\text{HCl}$, evaporating in a vacuum desiccator and cooling at -10° for some time, when white granular crystals of $\text{H}_4\text{P}_2\text{O}_7$, m.pt. 61° , separate (Giran, 1902). A crystalline hydrate $2\text{H}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ is described.

Pyrophosphates give a white precipitate of silver pyrophosphate $\text{Ag}_4\text{P}_2\text{O}_7$ with silver nitrate, but no precipitate with barium chloride except in alkaline solution. Magnesium pyrophosphate is formed on heating magnesium ammonium phosphate: $2\text{MgNH}_4\text{PO}_4 = \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$.

If a solution of pyrophosphoric acid is kept for some time, or is boiled,

orthophosphoric acid is formed : $\text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$, but the salts are very stable in solution.

Pyrophosphoric acid is tetrabasic and is stronger than orthophosphoric acid :

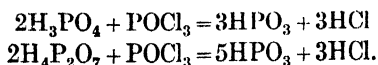
$$\begin{aligned} K_1 &= [\text{H}^+][\text{H}_3\text{P}_2\text{O}_7']/[\text{H}_4\text{P}_2\text{O}_7] = 1.4 \times 10^{-1} \\ K_2 &= [\text{H}^+][\text{H}_2\text{P}_2\text{O}_7'']/[\text{H}_3\text{P}_2\text{O}_7'] = 1.1 \times 10^{-2} \\ K_3 &= [\text{H}^+][\text{HP}_2\text{O}_7''']/[\text{H}_2\text{P}_2\text{O}_7''] = 2.7 \times 10^{-7} \\ K_4 &= [\text{H}^+][\text{P}_2\text{O}_7'''']/[\text{HP}_2\text{O}_7'''] = 2.4 \times 10^{-10} \end{aligned}$$

Only two series of salts are common, the normal salts $\text{M}_4\text{P}_2\text{O}_7$ and the diacid salts $\text{M}_2\text{H}_2\text{P}_2\text{O}_7$. Examples are $\text{Na}_4\text{P}_2\text{O}_7, 10\text{H}_2\text{O}$; $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$; $\text{Ca}_2\text{P}_2\text{O}_7, 4\text{H}_2\text{O}$; $\text{Ag}_4\text{P}_2\text{O}_7$ (insoluble), and $\text{Ag}_2\text{H}_2\text{P}_2\text{O}_7$ (soluble). The intermediate salts $\text{NaH}_3\text{P}_2\text{O}_7$ and $\text{Na}_3\text{HP}_2\text{O}_7$ have been described. Complex ions containing metals (Ag, Zn, Pb, etc.) are formed by dissolving the insoluble metal pyrophosphates in alkali pyrophosphate solution.

Metaphosphoric acid is formed as a sticky mass when ortho- or pyrophosphoric acid is heated at 316° , best in a gold crucible (Graham, 1833): $\text{H}_3\text{PO}_4 = \text{HPO}_3 + \text{H}_2\text{O}$, or by heating ammonium phosphate: $(\text{NH}_4)_2\text{HPO}_4 = \text{HPO}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$. By prolonged heating to redness some phosphorus pentoxide seems to be formed, as the hard glass obtained on cooling crackles when thrown into water (Berzelius). The water content of the residue depends on the duration of heating, and pyrophosphoric acid is formed as an intermediate product. At a white heat the acid volatilises and the vapour density corresponds with $(\text{HPO}_3)_2$ (Tilden and Barnett, 1896). The freezing point of a solution of the glass in water shows that the acid is polymerised, $(\text{HPO}_3)_n$, whilst the acid in the solution prepared from lead metaphosphate and hydrogen sulphide has the simple formula HPO_3 .

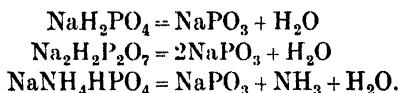
Holt and Myers (1911, 1913) by freezing-point measurements distinguished four varieties of metaphosphoric acid: (1) HPO_3 from the lead salt and H_2S , (2) the "crackling" acid, (3) the brittle non-deliquescent glass prepared by heating (2) to redness for twenty-four hours, $(\text{HPO}_3)_2$, and (4) the deliquescent glass obtained by heating the commercial acid for a short time, $(\text{HPO}_3)_3$.

Pure metaphosphoric acid is best obtained (Geuther, 1874) by the action of phosphorus oxychloride on crystalline ortho- or pyrophosphoric acid :



Metaphosphoric acid (unlike the other phosphoric acids) at once coagulates albumin (white of egg) and gives a white precipitate with barium chloride in *acid* solution. Silver nitrate gives a white amorphous precipitate of silver metaphosphate AgPO_3 from a nearly neutralised solution.

Sodium metaphosphate, probably the hexametaphosphate $(\text{NaPO}_3)_6$, is formed as a clear glass when acid sodium orthophosphate, acid sodium pyrophosphate, or microcosmic salt is heated to redness :



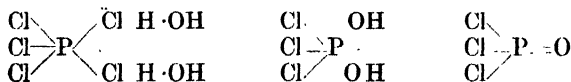
The metaphosphates are more numerous than the simple formula HPO_3 for the acid would suggest. Fleitmann and Henneberg (1848) regarded them as derived from polymerised metaphosphoric acids $(\text{HPO}_3)_n$, where $n = 1, 2, 3, 4$ and 6 . By heating NaH_2PO_4 at 315° Graham (1833) obtained a sparingly soluble metaphosphate, usually called *Maddrell's salt* (1847) and regarded as the monometaphosphate NaPO_3 . On further heating this gives a soluble trimetaphosphate $(\text{NaPO}_3)_3$, and a soluble tetrametaphosphate $(\text{NaPO}_3)_4$. When fused and rapidly cooled the metaphosphate forms a clear glass, m.pt. 640° , also obtained by heating microcosmic salt; this is called *Graham's salt*, is very soluble, and is the hexametaphosphate $(\text{NaPO}_3)_6$. From freezing-point and conductivity measurements Tammann (1890) concluded that it is complex, $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. It is used under the name *calgon* for softening water; the calcium is not precipitated but forms a complex ion which does not precipitate soap :



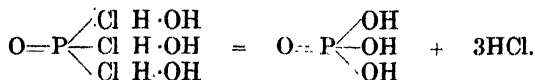
When Maddrell's salt or the tetrametaphosphate is carefully heated, a crystalline salt melting above 800° called *Kierul's salt* (1892) is formed; it is supposed to be the octametaphosphate $(\text{NaPO}_3)_8$. Pascal (1923-4), who prepared the monometaphosphate NaPO_3 by the action of sodium ethoxide on the ester $(\text{C}_2\text{H}_5\text{PO}_3)_6$, regarded Maddrell's salt as the dimetaphosphate $(\text{NaPO}_3)_2$.

Polyphosphates, e.g. $\text{Na}_6\text{P}_3\text{O}_{10}$ ($= \text{Na}_4\text{P}_2\text{O}_7 + \text{NaPO}_3$) are prepared by fusing pyro- and metaphosphates together.

Constitution of phosphoric acids.—From its method of preparation phosphorus oxychloride is given the formula $\text{O}=\text{P}(\text{Cl})_2$ with a double bond between the phosphorus and oxygen :



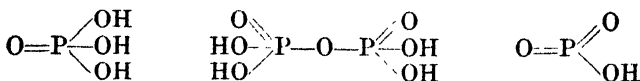
Since orthophosphoric acid is formed by the action of water on phosphorus oxychloride it probably contains the phosphoryl radical $\equiv \text{P}=\text{O}$:



In non-ionic reactions all three hydroxyl groups of orthophosphoric acid are substituted, as in the formation of the ester, triethyl orthophosphate $\text{O}=\text{P}(\text{OC}_2\text{H}_5)_3$.

The electronic formulae of the phosphoric acids have been repre-

serited as giving phosphorus a covalency of four. Phosphorus, unlike nitrogen, may have a covalency of five (as in PF_5 , PCl_5 , etc.), and the bond distances show that the formulae with double bonds :



are nearer the truth than those giving the octet structure with coordinate links instead of double bonds.

Perphosphoric acids.—Phosphates may crystallise with hydrogen peroxide : those with an acid reaction, such as primary phosphates (NaH_2PO_4 , etc.), either do not react or form very unstable compounds ; tertiary phosphates, with an alkaline reaction (K_3PO_4 , etc.) decompose hydrogen peroxide ; but the secondary phosphates and pyrophosphates of alkali metals give fairly stable crystalline compounds, e.g. $\text{K}_2\text{HPO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}_2$, $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}_2$, $\text{CaHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}_2$, $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. These are not true perphosphates. True perphosphates, which do not give reactions of hydrogen peroxide, are obtained in solution by the electrolysis of secondary phosphates of potassium, rubidium, caesium and ammonium in presence of fluorides and chromates, but not from lithium or sodium salts. They oxidise acidified manganous salt solutions to pink permanganic acid, and give a black precipitate with silver nitrate solution. These are salts of peridiphosphoric acid, $\text{H}_4\text{P}_2\text{O}_8$, and permonophosphoric acid, $\text{H}_5\text{P}_5\text{O}_{15}$.

Solutions supposed to contain H_3PO_5 and $\text{H}_4\text{P}_2\text{O}_8$ are formed by the action of 30 per cent hydrogen peroxide at low temperatures on phosphorus pentoxide, and on a large excess of pyrophosphoric acid, respectively.

Phosphorus trioxide.—The formation of a lower oxide of phosphorus by the slow oxidation of phosphorus in air or its combustion in a limited supply of air was noticed by Sage (1777), but pure phosphorus trioxide was first isolated by Thorpe and Tutton (1890-91). White phosphorus is burnt in a stream of air in a tube, the P_2O_5 also formed is removed by filtration through glass wool, and the phosphorus trioxide vapour is condensed by cooling.

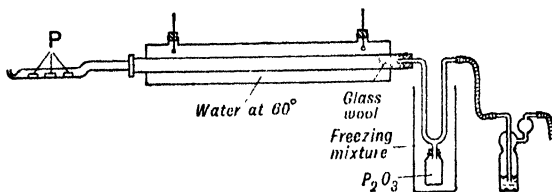


FIG. 303.— Preparation of phosphorus trioxide.

Sticks of phosphorus $1\frac{1}{2}$ in. long are placed in a hard glass tube (Fig. 303) connected with the brass inner tube, 1 in. in diameter and 2 ft. long, of the Liebig's condenser containing water at 60° . A plug of glass wool in the brass tube at the end farthest from the phosphorus serves to filter out solid P_4O_{10} , whilst the P_2O_5 vapour passing on is condensed in the U-tube.

immersed in ice. A rapid stream of air is aspirated through the apparatus by a water-pump connected with a sulphuric acid wash-bottle, and the phosphorus ignited. The trioxide condensed in the U-tube is melted by warming and runs down into the small bottle beneath.

Pure phosphorus trioxide is a colourless crystalline (monoclinic) solid, m.pt. 23.8° , b.pt. 173.1° ; when impure it is waxy. The vapour density and the depression of freezing point of benzene correspond with the formula P_4O_6 .

The P_4O_6 molecule (like the As_4O_6 molecule, see p. 858) has the four phosphorus atoms at the corners of a tetrahedron, each linked to three oxygen atoms along the tetrahedron edges (Fig. 304). The P to O distance indicates a large amount of double bond character, also shown by the

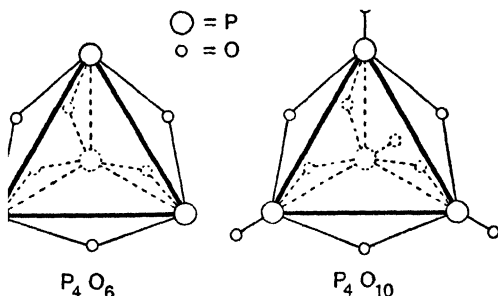


FIG. 304.—Structure of oxides of phosphorus.

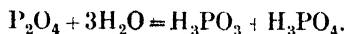
valency angle 125° for P—O—P. In P_4O_{10} an extra oxygen atom is added to each phosphorus atom, completing the PO_4 tetrahedra, these unshared oxygen atoms being very close to the phosphorus atoms. In the $P_4O_6S_4$ molecule, which has a similar structure, the P to S distance is short.

Unless quite pure, phosphorus trioxide slowly turns red in light owing to the conversion of white phosphorus contained as an impurity into red phosphorus, and it may be purified by repeated exposure to light and sublimation; when quite pure it does not glow in air (C. C. Miller, 1929). It has a pungent acid smell and is very poisonous. It oxidises in air or oxygen to the pentoxide, inflames at 70° in air and at 50° in oxygen, and spontaneously in chlorine, forming $POCl_3$ and another product, perhaps metaphosphoryl chloride PO_2Cl . It dissolves slowly in cold water, forming phosphorous acid: $P_2O_3 + 3H_2O = 2H_3PO_3$; with hot water an explosive reaction occurs, with formation of phosphine, phosphoric acid, and red phosphorus: $2P_2O_3 + 6H_2O = PH_3 + 3H_3PO_4$. Alkalis act similarly.

Phosphorus trioxide combines violently with sulphur to form crystalline $P_4O_6S_4$. Phosphorus trioxide inflames in contact with alcohol, but dissolves without decomposition in ether, carbon disulphide, benzene

and chloroform. With ammonia it probably forms the diamide of phosphorous acid $\text{HO}\cdot\text{P}(\text{NH}_2)_2$.

Phosphorus tetroxide.—Liquid phosphorus trioxide heated in a sealed tube is stable up to 200° ; at 210° it becomes turbid, and at 440° a sublimate of phosphorus tetroxide, discovered by Thrope and Tutton (1886), and a residue of red phosphorus are formed: $2\text{P}_4\text{O}_6 = 3\text{P}_2\text{O}_4 + 2\text{P}$. The tetroxide sublimes in vacuum at 180° . The vapour density at 1400° corresponds with P_8O_{16} . If phosphorus is burnt in a limited supply of air in a tube a buff-coloured powder deposits on the cooler part, which is a mixture of red phosphorus, P_2O_5 and P_2O_3 . On heating in a sealed tube at 290° this gives a crystalline sublimate of phosphorus tetroxide: $\text{P}_2\text{O}_3 + \text{P}_2\text{O}_5 = 2\text{P}_2\text{O}_4$. With water, P_2O_4 gives a mixture of phosphorous and phosphoric acids:

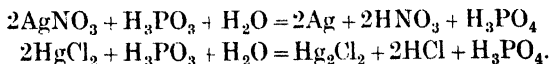


Phosphorous acid is formed when phosphorus trioxide is dissolved in cold water, but is most conveniently prepared by the action of water on phosphorus trichloride (Davy, 1812): $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$.

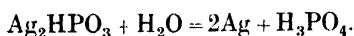
To minimise the rise in temperature the trichloride may be added to concentrated hydrochloric acid, when hydrogen chloride gas is evolved and the heat of solution of this does not appear. The solution is evaporated until the temperature rises to 180° , when hydrogen chloride is driven off, and the phosphorous acid is crystallised by cooling. The crystalline acid is also obtained by heating phosphorus trichloride with oxalic acid crystals until frothing ceases, and cooling (Hurtzig and Geuther, 1859): $\text{PCl}_3 + 3(\text{COOH})_2 = \text{H}_3\text{PO}_3 + 3\text{CO} + 3\text{CO}_2 + 3\text{HCl}$.

Phosphorous acid forms white deliquescent crystals, m.pt. 73.6° , decomposing at 200° into phosphine and phosphoric acid: $4\text{H}_3\text{PO}_3 = \text{PH}_3 + 3\text{H}_3\text{PO}_4$; in air the phosphine burns with bright flashes.

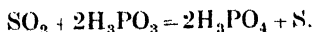
Phosphorous acid is a fairly strong reducing agent, precipitating some metals, such as gold and silver, from solutions of their salts, and reducing mercuric to mercurous chloride:



Silver nitrate with a phosphite gives first a white precipitate of silver phosphite, Ag_2HPO_3 , which soon turns black from formation of silver:

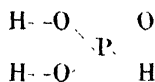


Phosphorous acid precipitates sulphur from sulphurous acid (some pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$, is also formed):



It is slowly oxidised by iodine and by permanganate in solution.

Phosphorous acid is *dibasic* (Wurtz, 1845); although normal esters $P(OR)_3$ are known the ordinary salts are M_2HPO_3 , where M is a univalent metal. The dibasic character is explained by the formulation :



the reducing properties being due to the hydrogen atom directly attached to the phosphorus. The acid is rather weak. The two series of phosphites known are MH_2PO_3 and M_2HPO_3 . When boiled with alkalis they do *not* evolve hydrogen (cf. hypophosphites), but they evolve phosphine with zinc and dilute hydrochloric acid. Ordinary sodium phosphite is $Na_2HPO_3 \cdot 5H_2O$, the calcium salt is $2CaHPO_3 \cdot 3H_2O$.

Phosphorous acid reacts with phosphorus pentachloride in the normal manner: $H_3PO_3 + 3PCl_5 = PCl_3 + 3POCl_3 + 3HCl$.

Pyrophosphorous acid $H_4P_2O_6$ is formed in needles, m.pt. 38° , by shaking PCl_3 with H_3PO_3 for five hours at $30-40^\circ$, and leaving in a desiccator over KOH and P_2O_6 . **Metaphosphorous acid** HPO_2 is formed in feathery crystals by the oxidation of phosphine by oxygen under 25 mm. pressure: $PH_3 + O_2 = HPO_2 + H_2$.

Hypophosphoric acid.—If sticks of phosphorus in glass tubes open at both ends are supported in a glass funnel over water under a bell-jar



FIG. 305.—Preparation of hypophosphoric acid.

(Fig. 305), oxidation occurs and fumes sink and dissolve in the water. Dulong (1816) noticed that the acid made in this way, called "Pelletier's phosphorous acid" (1796), differs from ordinary phosphorous acid, and he called it "phosphatic acid." Salzer (1877) found that if the liquid is partly neutralised with soda, sparingly soluble crystals of $Na_2H_2P_2O_6 \cdot 6H_2O$ slowly separate. If lead nitrate is added

to a solution of this, $Pb_2P_2O_6$ is precipitated, and on suspending this in water and passing in hydrogen sulphide, a solution of hypophosphoric acid is obtained, which on evaporation in a vacuum desiccator over sulphuric acid gives crystals of $H_4P_2O_6 \cdot 2H_2O$, m.pt. 62° , which lose water, forming $H_4P_2O_6$, m.pt. 70° .

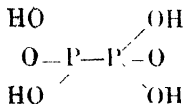
In another preparation (Corney, 1882) 6 gm. of silver nitrate dissolved in 100 gm. of nitric acid diluted with its own volume of water is heated with 9 gm. of white phosphorus. When the violent reaction subsides the

solution is filtered and cooled, when silver hypophosphate $\text{Ag}_4\text{P}_2\text{O}_6$ separates. This is decomposed by hydrochloric acid to form hypophosphoric acid.

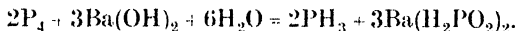
Hypophosphates are formed by the action of bleaching powder or sodium hypochlorite solutions on red phosphorus (Speter, 1927; Probst, 1929), and the acid by oxidising phosphorous acid with iodine (Kolthovska, 1937).

Hypophosphoric acid decomposes on heating: $\text{H}_4\text{P}_2\text{O}_6 = \text{H}_3\text{PO}_3 + \text{HPO}_3$, and at 180° phosphine is evolved. It differs from phosphorous acid in having no reducing action on metallic salts and in not being reduced by nascent hydrogen. The thorium salt is sparingly soluble. The acid is oxidised by hot permanganate, but only slowly by cold.

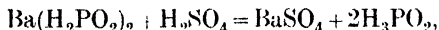
The doubled formula of the acid $\text{H}_4\text{P}_2\text{O}_6$ is confirmed by the existence of an acid sodium salt $\text{Na}_3\text{HP}_2\text{O}_6 \cdot 9\text{H}_2\text{O}$, and the molecular weight of the ester $(\text{C}_2\text{H}_5)_4\text{P}_2\text{O}_6$ in solution (Arbusov and Arbusov, 1931). The structural formula is probably:



Hypophosphorous acid.—The residue from the preparation of phosphine by heating white phosphorus with alkali hydroxide solution (p. 571) contains a salt of hypophosphorous acid (Dulong, 1816). A solution of barium hypophosphite is made by heating white phosphorus with baryta water:



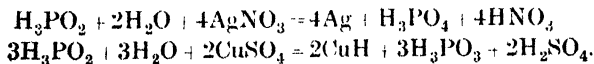
It is filtered from barium phosphate also formed and the excess of baryta is removed by precipitation as barium carbonate by a current of carbon dioxide. The barium hypophosphite is recrystallised as $\text{Ba}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$. A solution of barium hypophosphite is precipitated with the calculated amount of dilute sulphuric acid:



and the filtered solution of the acid carefully evaporated below 130° to a syrup, and cooled in a freezing mixture, when it crystallises. A 10 per cent solution of the acid is made commercially.

Hypophosphorous acid forms colourless crystals, m.pt. $26 \cdot 5^\circ$, decomposing at 130° , becoming yellow and evolving phosphine: $3\text{H}_3\text{PO}_2 = 2\text{H}_3\text{PO}_3 + \text{PH}_3$. The salts also evolve phosphine on heating.

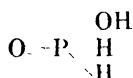
Hypophosphorous acid and hypophosphites are powerful reducing agents, precipitating many metals, *e.g.* silver, from solutions of their salts. Copper salts give on warming a brown precipitate of cuprous hydride:



Hypophosphorous acid and its salts may be titrated with acid permanganate :



Hypophosphorous acid is *monobasic*, forming crystalline salts such as sodium hypophosphite $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, and calcium hypophosphite $\text{Ca}(\text{H}_2\text{PO}_2)_2$, prepared by heating white phosphorus with sodium hydroxide solution or milk of lime, respectively, and used medicinally as tonics. Most hypophosphites are soluble in water (Th and Bi salts are insoluble). The acid may be formulated :

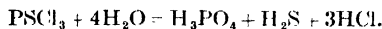


the reducing properties being due to the two hydrogen atoms directly attached to phosphorus, and the acidic properties to the single OH radical.

Phosphorus sulphides.—White phosphorus and sulphur react with explosive violence when fused together, but when a mixture of red phosphorus and small pieces of roll sulphur is heated in a loosely-corked flask reaction commences and proceeds without further heating. According to the proportions taken the phosphorus sulphides P_2S_5 , P_4S_7 , and P_4S_3 are obtained. A sulphide P_3S_6 has also been described. The pure pentasulphide P_2S_5 is a pale-yellow solid melting at 290° and boiling at 513° – 515° giving the normal vapour density; it is slowly hydrolysed by cold water: $\text{P}_2\text{S}_5 + 8\text{H}_2\text{O} = 2\text{H}_3\text{PO}_4 + 5\text{H}_2\text{S}$. It can be purified by recrystallising from carbon disulphide and heating at 150° in carbon dioxide to remove the solvent. The trisulphide P_4S_3 is purified by crystallisation from carbon disulphide or distillation in vacuum. P_4S_3 is bright-yellow, melts at 172.5° , boils at 408° giving the normal vapour density, and is only slowly hydrolysed by hot water. The heptasulphide P_4S_7 forms slightly-yellow crystals, sparingly soluble in carbon disulphide, m.pt. 310° , b.pt. 523° , rapidly hydrolysed by water.

Thiophosphoric acids.—Sodium salts of monothiophosphoric acid H_3PSO_3 , dithiophosphoric acid $\text{H}_3\text{PS}_2\text{O}_2$, and trithiophosphoric acid $\text{H}_3\text{PS}_3\text{O}$, are formed by adding phosphorus pentasulphide to sodium hydroxide solution and precipitating by alcohol. At 20° the trithiophosphate, at 50° the dithiophosphate $\text{Na}_3\text{PS}_2\text{O}_2 \cdot 11\text{H}_2\text{O}$, and at 90° the monothiophosphate $\text{Na}_3\text{PSO}_3 \cdot 12\text{H}_2\text{O}$, are formed. These precipitate barium; barium and strontium; and calcium, barium, and strontium salts, respectively. Magnesium ammonium thiophosphates are sparingly soluble in dilute ammonia. Dithiophosphates give a green colour with manganese and cobalt salts; cobalt monothiophosphate is intensely blue and the nickel salt is bright green.

Thiophosphoryl chloride PSCl_3 (Serullas, 1829) is a colourless fuming liquid, b.pt. 125° , formed by the reaction $\text{P}_2\text{S}_5 + 3\text{PCl}_5 = 5\text{PSCl}_3$. It is hydrolysed by water :



Thiophosphoryl fluoride PSF_3 (Thorpe and Rodger, 1888) is a colourless spontaneously inflammable gas, b.pt. -62.6° , formed by the reaction $\text{P}_2\text{S}_5 + 3\text{PbF}_2 = 2\text{PSF}_3 + 3\text{PbS}$.

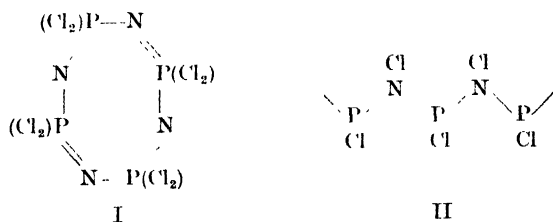
Compounds of phosphorus and nitrogen.—Phosphorus pentachloride reacts with dry ammonia gas forming a white solid mixture of substances containing $\text{PCl}_3(\text{NH}_3)_2$ (Gerhardt, 1846), which is converted by water into phosphamide $\text{PO}(\text{NH})\text{NH}_2$, a white insoluble powder. On heating the action of ammonia on PCl_5 in absence of air, **phospham** $(\text{PN}_2\text{H})_x$ remains as a white powder :



Phospham is only slowly oxidised on heating to redness in air, but is decomposed with incandescence by fused alkali, ammonia and a phosphate being formed. On heating in absence of air phosphamide gives a white powder of **phosphoryl nitride** : $\text{PO}(\text{NH})\text{NH}_2 = \text{PON} + \text{NH}_3$.

Ammonium chloride and phosphorus pentachloride at 175° – 200° form a mixture of six **phosphonitrile chlorides** : $(\text{PNCl}_2)_3$, $(\text{PNCl}_2)_4$, $(\text{PNCl}_2)_5$, $(\text{PNCl}_2)_6$, $(\text{PNCl}_2)_7$, and $(\text{PNCl}_2)_8$, which are very stable. The main product is $(\text{PNCl}_2)_3$, m.pt. 114° , b.pt. 256° . Ether solutions of these compounds when shaken with water form **metaphosphimic acids**, $[\text{HO}(\text{NH} : \text{PO})]_n$, stable salts of which, e.g. $(\text{NH}_4)_3\text{H}_3\text{P}_3\text{N}_3\text{O}_6 \cdot 12\text{H}_2\text{O}$, are known.

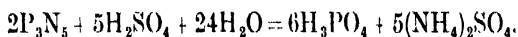
X-ray examination shows that $(\text{PNCl}_2)_3$ and $(\text{PNCl}_2)_4$, which form lustrous colourless crystals from benzene solutions, have ring structures. $(\text{PNCl}_2)_3$ forms an 8-membered zig-zag ring (like α -sulphur, p. 451), containing alternate nitrogen and phosphorus atoms with Cl_2 attached to P and with resonance among single and double bonds (I). The polymer



$(\text{PNCl}_2)_x$ is a colourless elastic rubber-like mass, probably (like plastic sulphur, p. 453) containing long chains of alternate phosphorus and nitrogen atoms, each linked to a chlorine atom (II).

Three **phosphorus nitrides** are described. The compound P_3N_5 is formed by heating P_2S_5 at 230° in ammonia and then in a current of hydrogen at a bright-red heat. When phospham is heated in vacuum above 400° it yields pure P_3N_5 by the reaction : $3\text{PN}_2\text{H} = \text{P}_3\text{N}_5 + \text{NH}_3$. P_3N_5 is a white amorphous powder, decomposing into its elements at high temperature in vacuum. It is scarcely affected by boiling water but is completely decomposed into

ammonia and phosphoric acid by water at 180°. It inflames when heated in oxygen or chlorine and is decomposed by many metals. P_3N_5 is decomposed by boiling concentrated sulphuric acid :



In vacuum at 730° it forms PN, which sublimes. PN exists in two forms, a red and a yellow. When the product of the reaction of liquid ammonia and PCl_3 is heated in vacuum at 550°, P_4N_6 , a white insoluble non-volatile spontaneously inflammable substance, is formed : at 750° in vacuum this gives a sublimate of PN (Moureu, etc., 1934-36).

CARBON AND HYDROCARBONS

Carbon and its compounds.—Carbon occurs in Nature both free and in combination. The element occurs in the crystalline forms of *diamond* and *graphite* (also called *plumbago* and *black-lead*), and amorphous *anthracite coal*. Free carbon (as diamond and graphite) also occurs in some meteorites, and the spectroscope shows that carbon is present in the sun and some stars. Mixtures of hydrocarbons compose mineral oil or *petroleum*. Coal contains complex hydrocarbons, but oxygen and nitrogen are also present. Carbon dioxide (CO_2) occurs uncombined in the atmosphere and combined as carbonates, especially calcium carbonate (CaCO_3) (*chalk*, *limestone*, and *marble*), magnesium carbonate MgCO_3 (*magnesite*), and a compound of the two CaCO_3 , MgCO_3 (*dolomite*) of which whole mountain-chains are constituted.

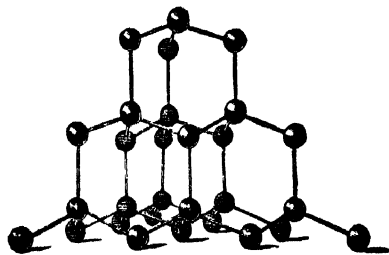


FIG. 306. The linking of carbon atoms in diamond.

Plants and animals contain *organic compounds* of carbon with hydrogen and oxygen, and sometimes nitrogen, sulphur, and phosphorus.

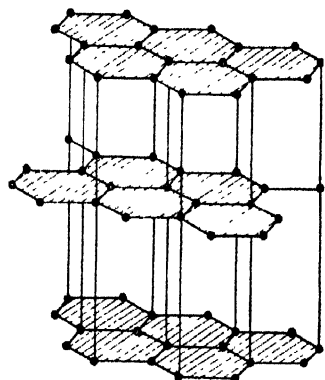


FIG. 307.—The linking of carbon atoms in graphite

The great number of these compounds (many of which have been prepared by synthesis from the elements) makes it necessary to study them in a special branch of the science called Organic Chemistry.

Carbon forms such a large number of compounds owing to the ease with which its atoms, unlike those of most other elements, combine to form chains (*aliphatic compounds*), or rings (*cyclic compounds*).

By means of X-rays the arrangement of the carbon atoms in diamond and graphite has been found; the lattices are described on pp. 391-2, and are shown (the diamond lattice redrawn) in Figs. 306 and 307. It will be seen that each atom is linked to four others.

In diamond the bonds are all the same length (1.5 Å.) and arranged tetrahedrally (*i.e.* the bonds from each atom point to the corners of a

regular tetrahedron with this atom at the centre). In graphite the arrangement is quite different: the carbon atoms are arranged in regular hexagons in flat parallel sheets, each atom being linked by strong bonds to three others at distances of 1.4 Å.

The sheets are 3.4 Å. apart and the fourth valency distance is so long that it may not be a real bond, but may be taken up in resonance between single and double bonds in the planes.

The strong bonds in diamond are supposed to account for its great hardness; the planes in graphite crystals readily slip, so that graphite easily flakes into thin films.

Allotropic forms of carbon.—Carbon is a striking example of allotropy. Most organic compounds when heated without access of air blacken or char, evolve steam and various volatile organic compounds and usually inflammable gases (*e.g.* methane CH_4), leaving finally a black residue of *charcoal*, which consists almost solely of carbon. The smoke produced on burning oils with a limited supply of air also consists mainly of particles of carbon. That charcoal should be chemically the same as diamond would appear improbable; its analogy with graphite or black-lead would seem clearer, yet it is curious that the composition of diamond was discovered (1772) before that of graphite (1800). The identity of the three forms of carbon was proved by showing that equal weights of the pure substances, when burnt in oxygen yield identical weights of carbon dioxide. The amounts of heat liberated are different: for 12.01 gm. of carbon they are: graphite 94.26 k. cal., diamond 94.43 k. cal., charcoal about 96.72 k. cal. These differences are supposed to be due to different modes of linkage of the carbon atoms. Since it has been shown by X-rays that all forms of charcoal (previously called "amorphous") consist of very minute crystals of graphite, *there are really only two true allotropic forms of carbon, diamond and graphite.*

Diamond.—Diamonds are found in India, Brazil, British Guiana, New South Wales, and particularly in South Africa. Most diamonds are small but the Cullinan diamond, discovered at Kimberley in 1905, weighed about $1\frac{1}{2}$ lb., or 3032 carats (1 *carat* = 0.2054 gm. The International carat = 0.200 gm.). This is the largest yet discovered, and was cut into two brilliants of 516.5 and 309 carats. The South African mines supply over 96 per cent of the diamonds of the world.

Large colourless diamonds are the Pitt diamond (136.25 carats), and the Koh-i-noor, originally 186 carats but reduced to 106 by recutting. The Hope diamond, 44.5 carats, is a fine blue stone. The cause of the colour of diamonds is not clear: exposure to cathode rays may deepen the colour, which is lost on heating to 300° – 400° , except in the case of yellow, which is very stable.

Black or dark-coloured (green, brown, red or grey) diamonds, known as *carbonado* and *bort* (or *boart*) are of no value as gems but are very hard and are used for rock-drills, for lathe tools for setting abrasive wheels, for dies for wire-drawing (*e.g.* tungsten filaments for lamps), and when crushed for cutting and polishing clear diamonds. The latter are pressed

against a revolving metal disc, covered with diamond powder and oil. Only about 42 per cent of the original weight remains after cutting.

Boart may mean any impure diamond or even fragments of gem diamonds. *Carbonado* is usually understood to mean a massive form, granular and without cleavage, or an impure aggregate of small crystals. According to Roth (1925) the heats of combustion of colourless diamond and *carbonado* are 7·873 k. cal. and 7·884 k. cal. per gm. respectively.

Diamond crystallises in the regular (or cubic) system ; forms related to the cube or octahedron, sometimes with curved faces, predominate (Fig. 308). The curved faces have been formed by growth and not by the action of a solvent (Tolansky and Wilcock, 1947). By cutting, the natural crystalline form is removed and an artificial shape, which gives rise to a large amount of internal reflexion, is substituted. The "brilliant" consists of one larger flat face, forming the base of a many-sided pyramid.

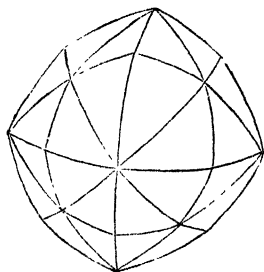


FIG. 308.—Diamond crystal.

Diamond is extremely hard, but fairly brittle : it is scratched by no other substance (except possibly boron carbide, B_4C) and stands highest in the *Mohs scale of hardness*, which comprises the following minerals :

- | | | | | |
|------------|--------------|----------------|------------|--------------|
| 1. Talc. | 3. Calcite. | 5. Apatite. | 7. Quartz. | 9. Corundum. |
| 2. Gypsum. | 4. Fluorite. | 6. Orthoclase. | 8. Topaz. | 10. Diamond. |

Each mineral in the scale is scratched by all those below it. In reality, diamond is about 140 times harder than corundum.

Diamond has a density of 3·510, a high refractive index (2·417 for the D-line), and a high dispersive power, giving a play of colours in white light. It is transparent to X-rays, whilst all imitations are opaque. Diamond is coloured green by α -rays from radium. Many diamonds phosphoresce in cathode rays or ultra-violet light. Diamonds are used for cutting glass ; for this purpose a chisel-shaped crystal edge is necessary, since a splinter merely scratches glass without cutting it.

Diamond resists nearly all chemical reagents ; a mixture of potassium dichromate and sulphuric acid oxidises it slowly at 200° to carbon dioxide. Diamond is attacked by fused sodium carbonate. Lebeau and Picon (1924) found that diamond is stable in a vacuum to 1500°, but at 1800° (more rapidly at 2000°) it is transformed into graphite. If heated at 900° in air or 700° in oxygen, diamond burns, clear diamond leaving only a trace of ash (0·05–0·2 per cent, chiefly silica and oxide of iron) while boart may leave as much as 4·5 per cent of ash. The ignition temperature of boart is higher than that of clear diamond.

The combustibility of diamond was foreshadowed by Newton, who, from the similarity of its refractive index to those of oil of turpentine, camphor and amber, suggested that it might be "an unctuous [oily] sub-

stance coagulated." The Florentine Academicians in 1694 heated a diamond in the focus of a powerful burning-glass : it glowed like a red-hot coal and disappeared. D'Arcet (1766) found that a diamond strongly heated in a *closed crucible* remained unchanged. Macquer (1771) found that a diamond strongly heated in air burns with a *small flame*, and Moissan (1896) said diamond burns in oxygen with "a very distinct flame." Allen and Pepys (1807) burnt diamond in oxygen and showed that it forms the same weight of carbon dioxide as charcoal. Davy (1814), using the original Florentine lens, burnt a diamond in oxygen. It took fire and continued to burn, even if removed from the focus, with a steady brilliant light. Nothing was produced but carbon dioxide, which rendered lime-water milky. Smithson Tennant (1797) burnt diamonds by strongly heating them in a gold tube with fused nitre (first used for this purpose by Guyton de Morveau, 1785) : he found that as much carbon dioxide was formed as Lavoisier (1772) had obtained from an equal weight of charcoal.

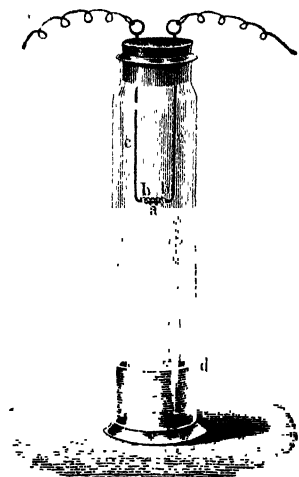


FIG. 309.- Combustion of a diamond in oxygen.

The combustion of a diamond in oxygen may be exhibited by heating a splinter of *carbonado* by an electric current in a spiral of fine platinum wire supported by copper leads inside a jar of oxygen (Fig. 309). A little lime-water is shaken up with the gas afterwards.

After many unsuccessful attempts, artificial diamonds were made by Moissan in 1893. He heated charcoal at a very high temperature with iron in a carbon crucible in an electric furnace, in which an electric arc is struck between carbon rods inside blocks of lime (Fig. 310). Fused iron dissolves carbon ; on cooling slowly most of the carbon deposits as scales of graphite, which are seen in a broken piece of grey cast-iron. On rapid cooling under ordinary conditions, the carbon remains in solid solution and white cast-iron is produced. Moissan cooled the iron containing carbon suddenly from 3500° by plunging the crucible into water. On dissolving the iron with hydrochloric acid, a residue was left containing three varieties of carbon : (1) a small amount of graphite, (2) curious brown twisted threads, apparently formed under great pressure, and (3) a portion denser than 3.4 which contained very small diamonds, some black and some transparent, which were isolated by careful purification and analysed by combustion.

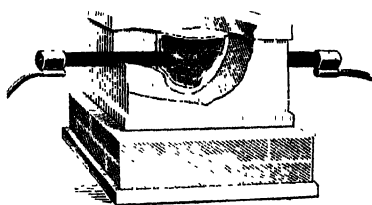


FIG. 310. - Moissan's electric furnace.

Moissan at first thought that the important condition was the enormous pressure developed by the solidification of the molten cast-iron inside the rigid outer skin, but he afterwards thought rapid cooling was the essential condition. Moissan's experiment was successfully repeated by Ruff (1917), who proved that the crystals were diamonds by several tests. The largest artificial diamond obtained measured 0.7 mm.

The presence of oxide of iron in diamond-bearing earth suggests that a process similar to that used by Moissan may have been responsible for the origin of the natural diamonds. Small clear diamonds have been found in meteorites, and diamonds may be of celestial origin: the iron may, however, have come from the interior of the earth.

Graphite.—Before 1779 molybdenum sulphide (MoS_2) and graphite (C) were confused under the name *molybdena* or *black-lead*, since both are soft grey minerals with a metallic lustre, giving a streak on paper like that produced by lead. Scheele in that year found that the first mineral gave a peculiar solid acid (molybdic acid, MoO_3) when roasted in the air, evolving sulphur dioxide. The name molybdena was reserved for this mineral, whilst the other was called graphite (Greek *grapho*—I write: the name is due to Werner), plumbago, or black-lead. It was thought to be a carbide of iron, since it usually left a residue of oxide of iron when burnt, carbon dioxide being formed. Scheele noticed that graphite deposits from molten iron in blast furnaces: this variety is called *kish*. In 1802 Clement and Desormes burnt graphite in oxygen and found that it gave as much carbon dioxide as an equal weight of pure charcoal. Very pure graphite was prepared by Brodie in 1855.

Graphite is found in Borrowdale in Cumberland (the mines are worked out), Siberia, Bohemia, Bavaria, and Ceylon, and there is some in Canada, California, and New York State. Ceylon graphite is purest, but Siberian and Bohemian varieties are most used for making pencils.

Artificial graphite is made by the Acheson process (1896) at Niagara. A mixture of sand and powdered anthracite or coke (petroleum coke is best) is heated very strongly for twenty-four to thirty hours by an electric current. Carbon rods lead the current through the mass, which is supported on a brick furnace and covered with sand (Fig. 311).

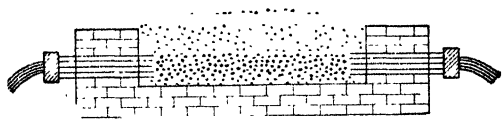


FIG. 311 Production of graphite in the electric furnace.

Artificial graphite is very pure and soft, and free from grit, but is more expensive than natural graphite. It is used for electrodes, brushes, carbons for dry batteries, and as a lubricant, but not for pencils. With water containing tannin it forms a colloidal suspension used as a lubricant called *deflocculated graphite* or "aquadag": when kneaded with oil, the water is squeezed out and the suspension of graphite in oil is called "oidag" ("dag" = deflocculated Acheson graphite).

Graphite crystallises in grey shining plates belonging to the hexagonal or trigonal crystal system, but is usually found in masses of easily separated thin sheets, which when rubbed flake off in thin layers; hence it has a greasy feel, makes a streak on paper, and acts as a lubricant. It is also used (as "black-lead") in polishing iron work and granular gunpowder. Pure graphite has a density of 2.25. Graphite is a good conductor of heat and electricity, hence it is used in the cores of arc-carbons, as anodes for electrolytic cells and for covering plaster moulds on which copper is deposited by electro-deposition.

Graphite burns only at a high temperature (about 690° in air), and is used for making plumbago crucibles: these consist of 75 parts of plastic clay, 25 of sand, and 100 of graphite, moulded and baked. A granular mixture of graphite, silicon carbide, and clay is used as a resistance (*kryptol*) in electric furnaces. Mixed with a little plastic clay and squirted into threads, graphite is used to make black-lead pencils. Conrad Gesner in 1565 described a lead pencil made with *stimmi Anglicum*, i.e. Borrowdale graphite.

Graphite is not attacked by dilute acids or fused alkalis, or when heated in chlorine. A mixture of potassium dichromate and sulphuric acid slowly oxidises it to carbon dioxide. It burns brilliantly in fused nitre at a high temperature. Graphite is not attacked by fused sodium sulphate, which dissolves coke and retort carbon, but gives carbon monoxide with fused sodium carbonate. When finely granulated, moistened with fuming nitric acid, and heated, some varieties (Siberian and Austrian) do not swell, whilst others (Ceylon and American) do. This is *Luzi's test* (1891).

Graphitic oxide.-Charcoal slowly dissolves in hot dilute nitric acid forming a brown substance called "artificial tannin" by Hatchett (1805). Alkaline permanganate oxidises charcoal to oxalic acid and mellitic acid, $C_6(COOH)_6$, a derivative of benzene, the aluminium salt of which is the mineral mellitite or honey-stone. Graphite is oxidised by a mixture of nitric acid, potassium chlorate and concentrated sulphuric acid to a peculiar, almost insoluble, solid called *graphitic acid* (Brodie, 1859) or *graphitic oxide* (Berthelot, 1869). The formation of graphitic acid has been regarded as a test for graphite, but small amounts have been obtained from some kinds of so-called "amorphous" carbon.

One gm. of pure powdered Ceylon graphite is added to a cooled mixture of 40 ml. of conc. H_2SO_4 and 20 ml. of 60 per cent HNO_3 . To the mixture are added, in small portions over a period of 1½ hours, 20 gm. of $KClO_3$, with shaking. The mixture is allowed to stand 16 hours and then poured into 1 litre of distilled water. The graphitic acid is washed by decantation till free from acid, filtered (it is difficult to filter) and dried in a desiccator over P_2O_5 , when it forms a mass like varnish (U. Hofmann, 1928).

According to Brodie and Berthelot, pure graphitic acid is bright yellow when moist. The crude greenish product is purified by treatment with acidified permanganate. It is brown when dry.

Graphitic oxide is very sparingly soluble in pure water but reddens moist litmus paper: it is amorphous in appearance, but the X-rays

show that it is crystalline. According to Brodie its formula is $C_{11}H_4O_5$. On heating it decomposes violently at 200° and leaves a fine black powder of *pyrographitic oxide*, $C_{22}H_2O_4$ (?). When heated with hydriodic acid in a sealed tube, graphitic oxide takes up hydrogen, forming *hydrographitic acid*, which does not yield pyrographitic oxide on heating. Graphitic oxide appears to contain a graphite lattice with oxygen atoms attached to carbon. The ratio C : O may be as high as 4 : 1 but is usually about 2 : 1. The exact structure is unknown.

A mixture of potassium chlorate and concentrated sulphuric acid converts graphite into a purple substance containing hydrogen, oxygen and sulphuric acid, called *graphon sulphate* by Brodie. On heating, this swells up, evolves gas, and falls to a fine powder of *pure graphite* (density 2.25). If this is thrown on water, the impurities sink and the pure graphite remains floating on the surface.

Other coloured graphite salts with nitric, perchloric, and pyrophosphoric acids have been described (Hofmann, 1938): the acid radicals (HSO_4' , NO_2' , P_2O_7'''') seem to be contained in the spacings between the sheets of carbon atoms in the graphite lattice.

Charcoals.—The following varieties of "amorphous" carbon are usually described; as stated above, they all consist of very minute crystals of graphite in irregular orientation. They are all black and opaque, the density and hardness depending largely on the temperature at which they were formed.

1. **Charcoal**, from wood, sugar, etc. 2. **Lampblack**, soot, acetylene black. 3. **Animal charcoal**, bone-charcoal, ivory black. 4. **Coke** (also anthracite, etc.). 5. **Gas carbon**. 6. **Electrode carbon**, arc carbons, etc.

The black residue rich in carbon, obtained by heating vegetable substances such as wood or sugar with exclusion of air, is known as *charcoal*. The purest variety is obtained by heating recrystallised cane-sugar in a large covered crucible until gas ceases to be evolved; the resulting charcoal is heated at 1000° in a graphite tube in a current of chlorine to remove residual hydrogen as hydrogen chloride, after which it is washed and heated strongly in hydrogen to remove chlorine. Charcoal so prepared has a density of 1.8, and ignites in air at 450° . Charcoal free from hydrogen is also produced, mixed with magnesia, by burning magnesium in carbon dioxide.

The low ignition temperature in oxygen of wood charcoal as compared with the other forms of carbon is seen from Moissan's results :

	Diamond	Graphite	Charcoal
Evolution of carbon dioxide begins -	720°	570°	200°
Evolution of carbon dioxide abundant	790°	600°	—
Burns with flame - - - -	800°	850°	690°
			345°

Wood charcoal is prepared by the thermal decomposition of wood into volatile parts (gas, water, acetic acid, acetone, methyl alcohol and tar), and nonvolatile charcoal.

Dry wood on heating to 220° becomes brown, at 280° deep brown, at 310° black and friable; above 350° black charcoal is produced. The distillation

of wood, with production of tar, acid, and spirit, was examined by Glauber in the seventeenth century. The percentage of carbon in good charcoal is about 93; it contains about 1.5 per cent of oxygen, 2.5 per cent of hydrogen and 3 per cent of ash. By heating above 1500° , the hydrogen falls to 0.62 per cent.

The manufacture of charcoal is carried out in (a) pits or heaps (*meiler*), (b) closed ovens or retorts. The charring in meiler is very old. A rough central chimney is built of turf, and billets of wood stacked round it in a conical pile, the whole being covered in with turf (Fig. 312). A lighted faggot is dropped down the chimney to kindle the wood, which

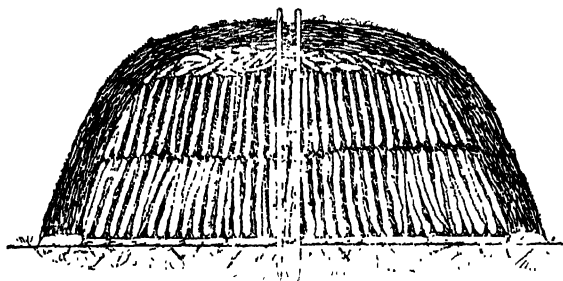


FIG. 312. Charcoal "Meiler."

burns *slowly*, just sufficient air being admitted through holes at the bottom. Part of the wood burns, and the heat generated chars the rest. After some days the luminous flame from the chimney is replaced by a blue flame of carbon monoxide. All the air-holes are now stopped up and the charcoal is allowed to cool. About 24 per cent of the weight of the wood is obtained as charcoal, all the volatile products are lost.

In the modern process the wood is heated in externally fired ovens or iron retorts, from which air is excluded. The volatile liquid products are collected, and the inflammable gas is used for heating the retorts. The liquid distillate consists of (a) a watery portion (*pyroligneous acid*) containing water, acetic acid, methyl alcohol, and acetone; (b) wood tar, which is valuable (e.g. Stockholm tar, from pinewood). The yields from 100 parts by weight of dry wood are: charcoal 25, tar 10, pyroligneous acid 40, gas 25.

Properties of charcoal.—Wood charcoal is black and friable, retaining the shape of the wood but smaller in volume. Although the density of air-free charcoal is 1.3-1.9, the mass is very porous and floats on water. If the air is removed by an air pump, charcoal in water in a bottle gives out bubbles and slowly sinks. Charcoal is very permanent on exposure to air and moisture; charred oak stakes of the Roman period planted in the bed of the Thames, were found nearly two thousand years later still sound at heart.

In virtue of its great porosity, charcoal readily adsorbs gases (Scheele, and Fontana, 1777).

A piece of red-hot wood-charcoal is passed into a tube of ammonia gas standing over mercury (Fig. 313); the gas is rapidly adsorbed. The charcoal is cooled by the mercury, and takes up about 90 times its volume of ammonia gas.

A very active charcoal is prepared by heating pieces of coconut shell under sand in a crucible; 1 volume quenched under mercury adsorbs the following volumes of gases (reduced to S.T.P.) at the ordinary temperature

Ammonia	-	171.7	Hydrogen phosphide	69.1
Cyanogen	-	107.5	Carbon dioxide	- - 67.7
Nitrous oxide	-	86.3	Carbon monoxide	- 21.2
Ethylene	-	74.7	Oxygen	- - - 17.9
Nitric oxide	-	70.5	Nitrogen	- - - 15

The preferential adsorption of ethylene by charcoal has been used to extract it from coal gas. Vapours of volatile liquids are adsorbed more readily than gases: the volumes of ammonia, carbon dioxide, steam and alcohol vapour adsorbed at 126.5 are 21.9, 16.6, 43.8, and 110.8, respectively. Generally speaking, the adsorption increases the nearer the gas or vapour is to its liquefaction point at the temperature of the experiment. McBain found that the amount of gas taken up increases slowly with time, due to a slow penetration of the condensed layer into the interior. At low temperatures the adsorbed amount increases rapidly (Dewar, 1904):

Gas	He	H ₂	A	N ₂	O ₂
0	2	4	12	15.5	18
185	15	135	175	155	230
					volumes at S.T.P.

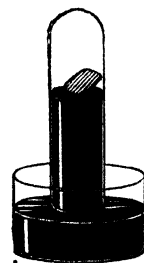


FIG. 313.- Absorption of ammonia gas by charcoal.

The condensed layer of gas held by the charcoal is very reactive. Lower a crucible containing warm powdered, recently ignited, charcoal into a jar of hydrogen sulphide. After it has become saturated with the gas, transfer it to a jar of oxygen. Ignition occurs (Stenhouse, 1855).

Chlorine adsorbed by charcoal combines with hydrogen in the dark; carbon monoxide and chlorine, or sulphur dioxide and chlorine, combine when passed over charcoal, which acts as a catalyst, to form carbonyl chloride (COCl₂), and sulphonyl chloride (SO₂Cl₂), respectively.

Charcoal also takes up many substances from solution, *e.g.* metallic salts, organic substances such as alkaloids (*e.g.* quinine), and colouring matters (Lowitz, 1790).

Boil solutions of litmus and indigo with finely-powdered animal charcoal, and filter. The filtrates are colourless.

A very active form of charcoal, "active charcoal," used in gas-masks, is obtained by heating charcoal (*e.g.* of birch wood) at 900° in a very limited supply of air or in steam, when the material obstructing the pores is removed. It is also obtained by carbonising wood which has been treated with salts

such as zinc chloride or magnesium chloride, which are removed from the charcoal by washing with water or acids. It adsorbs much more gas than ordinary charcoal. Active charcoal is also used (as well as animal charcoal and blood charcoal) in decolorising sugar syrup (Derosne, 1812), or for removing fusel oil from crude spirit.

The decolorising charcoal is revived by boiling it with caustic soda solution and washing. Bone black is revived by heating to redness in closed retorts.

Animal charcoal, also known as *bone-black*, is made by heating de-greased bones in iron retorts. The volatile products are (a) a watery liquid which (unlike that from wood) is alkaline and contains ammonia and nitrogenous organic bases, (b) gases, and (c) *bone-oil* or *Dippel's oil* (containing pyridine, etc.). The residue is a black mass containing 10 per cent of carbon in 80 per cent of calcium phosphate and calcium carbonate, etc. If the calcium salts are dissolved out by hydrochloric acid, the charcoal remains as *ivory black*.

Lampblack.—When coal, wax, oil, and turpentine burn with a supply of air insufficient for complete combustion, part of the carbon separates as a smoke which settles out as soot. A fine variety of soot called lamp-black is made by burning oil, tar, creosote oil, resin, etc., and collecting the soot on coarse blankets. In America, natural gas is burnt from steatite burners under a cooled rotating metal disc or rollers, or (usually) iron bands ("channels"), the whole being in an iron shed. The *gas black* (called *carbon black* in America) is removed by scrapers. A variety is made at Shawinigan by the explosion of acetylene (from refuse carbide) and air under pressures of 50–100 lb. per sq. in., or by burning the gas from burners. Most of the carbon black is used as a filler in rubber tyres, some as a pigment in printing ink, etc.

Lampblack contains oily impurities which may be removed by heating in chlorine; it is then a pure form of carbon, density 1.78.

Coal.—Some varieties of coal (anthracite) contain more than 90 per cent of carbon. Coal is a carbonaceous mineral which is the final result of a series of decompositions, in the presence of a limited supply of air, undergone by vegetable matter of the remote past. High pressure, due to the weight of superimposed strata, was probably also necessary. Part of the carbon, hydrogen, and oxygen came off as carbon dioxide, water, and methane (CH_4), and the residue became richer in carbon. The early stages of the decomposition were probably caused by bacteria, and heating under pressure may have played a part in the later stages. Vegetable remains in coal are seen with the microscope, and fossil trees and plants are often found in the coal seams. The kind of vegetable matter, and the way it was covered by earthy deposits, varied from case to case. Two theories have been proposed to explain the origin of coal. Large beds of coal are supposed to have been deposited *in situ* from vegetable remains; impure current-bedded local coal, such as cannel, is thought to be derived from the burying of water-borne vegetable matter in a delta.

Stokes, from microscopic investigations, recognised four constituents in banded coal: *durain*, *fusain*, *vitrain*, and *clarain*. Their behaviour on coking

(on heating out of contact with air) was shown by Lessing to be different. Fusain yields a powdery coke; durain coke is also very friable, whilst with clarain fusion and swelling occur, with formation of a brown coherent coke. Vitrain undergoes fusion, yielding a silver-white coke with excrescences. The four constituents have different adsorptive capacities for pyridine vapour.

The first stage in the conversion of vegetable matter into coal is supposed to be *peat*, which consists of accumulations of vegetable matter, chiefly mosses and bog-plants, which have undergone partial change but still preserve evidence of organic structure, although the deeper layers may be more compact and homogeneous. The next stage is represented by *lignite*, or *brown coal*, which is more compact than peat and is lustrous, although impressions and remains of vegetable fragments, leaves, etc., are still distinct and numerous.

The next stage of the process leads to the types of *bituminous coal*, i.e. common coal. Distinct evidences of fossilised vegetables are still present. Bituminous coals burn with a bright smoky flame, and are divided into *caking* and *non-caking* according as they do or do not soften and fuse together on burning or coking. *Cannel coal* is compact, dull grey or black, non-lustrous, breaking with a conchoidal fracture and giving gas and little coke on heating. Splinters of cannel coal burn like candles when ignited, hence the name. *Jet*, found at Whitby, etc., is a hard lustrous variety of cannel coal.

The last stage in coal-formation is *anthracite*, rich in carbon. Anthracite has a high ignition point, usually a brilliant lustre and a conchoidal fracture, and does not burn with a flame: it gives an intense heat on combustion, but is not suitable for ordinary grates. Anthracite occurs locally in many coal-fields, such as South Wales, Scotland, and Pennsylvania. *Graphite* may be the ultimate stage of decomposition, since it always contains a little hydrogen.

The following table shows the change in composition during the conversion of woody matter into coal, with the corresponding increase in calorific value.

	Carbon.	Hydrogen.	Oxygen.	Calorific Value B.Th U. per lb.
Wood - - - -	50.0	6.0	44.0	7,400
Peat - - - -	60.0	5.9	34.1	9,900
Lignite - - - -	67.0	5.2	27.8	11,700
Bituminous coal - - - -	88.4	5.6	6.0	14,950
Welsh steam coal - - - -	92.5	4.7	2.7	15,720
Anthracite - - - -	94.1	3.4	2.5	15,720
Pure charcoal - - - -	100.0	—	—	14,544
Petroleum - - - -	85.5	14.2	0.3	19,800
Coal gas - - - -	-	-	-	19,220
Hydrogen - - - -	-	100.0	—	62,100
Methylated spirit - - - -	52.2	13.0	34.8	11,160

(The values for wood, peat, etc., refer to materials free from moisture and ash; the actual materials contain water and the calorific values are

smaller than those given. The values for pure charcoal, coal gas, hydrogen, methylated spirit, and petroleum are given for comparison.)

The calorific value of a fuel is expressed as the number of British thermal units (B.Th.U., *i.e.* the number of lb. of water raised 1° F. in temperature) evolved by the complete combustion of 1 lb. of the fuel, the water formed being supposed condensed to the liquid state. It is determined by burning

a weighed amount of the fuel in compressed oxygen in a strong metal bomb calorimeter (Fig. 314). The fuel is ignited by a known weight of iron wire heated by an electric current and supported over a platinum spoon containing the fuel. The bomb is immersed in water in a calorimeter. The heat of combustion of the iron wire is subtracted from the total heat evolved.

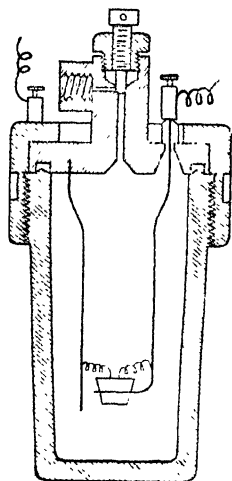


FIG. 314.—Bomb calorimeter.

Carbides.—Compounds of metals with carbon are called carbides. Of the alkali metals, only lithium combines directly with carbon, forming Li_2C_2 . Calcium is the only alkaline earth metal to combine directly with carbon, forming CaC_2 ; carbides of strontium and barium, SrC_2 and BaC_2 , are made by heating the oxides with carbon in the electric furnace: $\text{MO} + 3\text{C} = \text{MC}_2 + \text{CO}$. Beryllium combines directly with carbon, forming Be_2C . Of the earth metals, only aluminium unites with carbon to form Al_4C_3 ; the rest form carbides when their oxides are strongly heated with carbon. Manganese

and uranium form Mn_3C and UC_2 , which are decomposed by water.

By the action of water of some carbides, hydrocarbons are produced. Alkali and alkaline-earth carbides form *acetylene*: $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$. Beryllium and aluminium carbides give *methane*: $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$. Some carbides, *e.g.* thorium carbide ThC_2 , and uranium carbide UC_2 , form gaseous, liquid, and solid hydrocarbons: manganese carbide evolves a mixture of methane and hydrogen.

Metal carbides are divided into two classes: (i) *salt-like*, containing carbon anions (C^{2-} giving acetylene with water, C^{4-} giving methane) and metal ions; (ii) *refractory*, mostly very hard, with carbon atoms dispersed in the metal lattice (*e.g.* TiC , ZrC , VC , W_2C).

HYDROCARBONS.

Methane.—The *marsh gas* formed by the bacterial decay of vegetation (cellulose) at the bottom of marshy pools, and liberated in bubbles when the mud is disturbed with a stick consists mainly of methane and carbon dioxide. Methane occurs occluded in coal and escapes when the pressure is relieved, forming *fire-damp*, which when mixed with air causes explosions on ignition. The gas often issues in large quantities from "blowers" or fissures in the coal, and contains 80–98 per cent of

methane, with some carbon dioxide, ethane (C_2H_6), and nitrogen. *Natural gas* from petroleum wells contains more than 90 per cent of methane, and the gas from some kinds of rock salt is rich in methane.

Methane is formed by the direct combination of carbon and hydrogen at high temperatures: $C + 2H_2 \rightleftharpoons CH_4$. By circulating hydrogen over heated sugar-charcoal more than 95 per cent of the theoretical yield is produced. Between 1100° and 2100° , at pressures up to 200 atm., methane is the only saturated hydrocarbon formed: ethylene and acetylene are formed in smaller amounts. The percentages of methane in equilibrium with carbon and hydrogen at atmospheric pressure are: 850° , 2.5; 1000° , 1.1; 1100° , 0.6. Methane is produced when a mixture of hydrogen and carbon monoxide is passed over reduced nickel at 250° to 400° : $CO + 3H_2 = CH_4 + H_2O$.

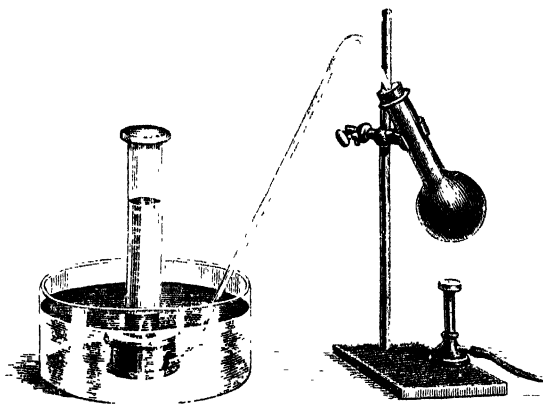
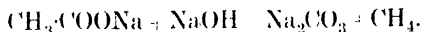


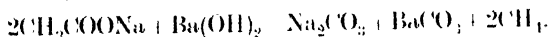
FIG. 315. Preparation of methane.

In the laboratory, methane is usually prepared by heating a mixture of sodium acetate, which has been fused to remove water of crystallisation, and powdered, with three times its weight of soda-lime in a hard glass or copper flask (Fig. 304):

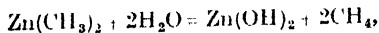


It is collected over water. Prepared in this way it is not very pure and may contain up to 8 per cent of hydrogen and 10 per cent of unsaturated hydrocarbons such as ethylene C_2H_4 , the presence of which causes it to burn with a slightly luminous flame.

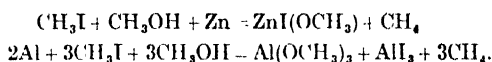
Nearly pure methane is obtained if anhydrous sodium acetate is heated with anhydrous barium hydroxide instead of soda-lime:



Pure methane is prepared by the action of water on zinc methyl:



or by the action of zinc-copper couple, or amalgamated aluminium, on a mixture of methyl iodide and methyl alcohol :



The zinc-copper couple is prepared by shaking dry zinc dust with one-tenth of its weight of dry copper oxide in a flask. The flask is fitted with a dropping funnel and a vertical tube containing granulated zinc which has been immersed in copper sulphate solution. A mixture of equal volumes of methyl iodide and methyl alcohol is dropped slowly on the couple, the flask being gently warmed if necessary. The methane passes through the coppered zinc, which frees it from methyl iodide vapour, and is then collected over water. Amalgamated aluminium is more active. It is made by immersing small pieces of sheet aluminium in mercuric chloride solution and washing in dry methyl alcohol. It is packed into a U-tube cooled in ice and is covered with methyl iodide. The mixture of methyl iodide and methyl alcohol is dropped on from a tap funnel fitted to one side of the U-tube and the gas evolved passes out through a delivery-tube.

Fairly pure methane is evolved by the action of water on aluminium carbide : $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} = 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$. It is purified from hydrogen by adding a little more pure oxygen than is necessary to combine with the hydrogen, and passing over palladium black or palladium asbestos at 100° . The excess of oxygen is then removed by alkaline pyrogallol.

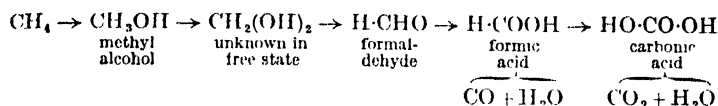
Properties of methane.—Methane is a colourless, odourless, non-poisonous gas, b. pt. -161.4° , m. pt. 185.8° . The critical temperature and pressure are -82.85° and 45.6 atm., the normal density 0.7168 gm./lit., slightly higher than the theoretical value of 0.7154 . It is sparingly soluble in water : 5.56 vols. in 100 vols. at 0° , and 3.3 vols. at 20° ; it is rather more soluble in alcohol.

Methane is very stable. It is decomposed by heat into carbon and hydrogen : the decomposition is inappreciable at 700° , and sixty times faster at 985° than at 785° . Reaction occurs on the surface of the vessel, a dense form of carbon being deposited. Methane burns in air or oxygen with a slightly luminous flame : $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$; its ignition point in air is high, viz. 650° – 750° . When mixed with oxygen or air it forms a violently explosive mixture : 1 vol. of methane requires 2 vols. of oxygen, or 9.5 vols. of air, for complete combustion. The lowest percentage of methane in air necessary for the propagation of flame is 5.6 by volume, and the lowest ignition temperature is stated to be 500° .

In the slow combustion of methane, when a mixture with air or oxygen is passed over heated porcelain, traces of formaldehyde $\text{H}\cdot\text{COH}$ are formed : $\text{CH}_4 + \text{O}_2 = \text{H}\cdot\text{COH} + \text{H}_2\text{O}$.

According to H. E. Armstrong, and Bone, the combustion of methane and of other hydrocarbons occurs by the entrance of oxygen into the molecule, where it is distributed between the carbon and hydrogen to form

unstable hydroxylated molecules which may undergo oxidation or thermal decomposition :

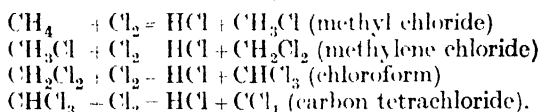


At 360° and 100 atm. pressure, up to 17 per cent of methane may rapidly be oxidised to methyl alcohol, with only 0.6 per cent to formaldehyde and no trace of hydrogen peroxide. Under ordinary conditions formaldehyde is the first product detected.

According to another theory, unstable peroxides are first formed and then decompose, the products being further oxidised by excess of oxygen into oxides of carbon and water.

Dalton (1805) found that when methane is mixed with its own volume of oxygen, "the least that can be used with effect," and fired by an electric spark, the mixture explodes without appreciable change in volume, with formation of carbon monoxide and hydrogen: $\text{CH}_4 + \text{O}_2 = \text{CO} + \text{H}_2 + \text{H}_2\text{O}$. "Each atom of gas requires only 2 atoms of oxygen; the one joins to one of hydrogen and forms water [HO, according to Dalton]; the other joins to the carbone to form carbonic oxide, and at the same moment the remaining atom of hydrogen springs off." On adding a further volume of oxygen, the gas may again be fired by a spark: $\text{CO} + \text{H}_2 + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$.

A mixture of 1 vol. of methane with 2 vols. of chlorine when kindled burns with a dull flame, producing fumes of hydrochloric acid and a black cloud of carbon: $\text{CH}_4 + 2\text{Cl}_2 = 4\text{HCl} + \text{C}$. A mixture of equal volumes of chlorine and methane on exposure to diffuse daylight, slowly reacts to form hydrogen chloride and *methyl chloride*: $\text{CH}_4 + \text{Cl}_2 = \text{CH}_3\text{Cl} + \text{HCl}$. With excess of chlorine, hydrogen is replaced by chlorine until *carbon tetrachloride* (CCl_4) is formed as a final product:



Mixtures of all the substances are usually produced. Since methane can react only by substitution or decomposition and not by addition, it is called a *saturated hydrocarbon*.

Ethylene.—Hydrogen and carbon at high temperatures react to form methane and a trace of ethylene, which may be absorbed by passing the cooled gas over charcoal cooled in liquid air. Most of the ethylene is decomposed at the high temperature. At 1200° the ratio of methane to ethylene is 100 : 1; at 1400° it is 10 : 1.

Ethylene is formed by passing alcohol vapour over thorium dioxide or alumina heated at 340°–350°, acting as a catalyst: $\text{C}_2\text{H}_5\text{OH} = \text{H}_2\text{O} + \text{C}_2\text{H}_4$.

Ethylene is prepared by dehydrating ethyl alcohol by means of zinc chloride, boron trioxide, phosphorus pentoxide, concentrated sulphuric acid, or syrupy phosphoric acid: $\text{C}_2\text{H}_5\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$. With sulphuric acid, ethylsulphuric acid, $\text{C}_2\text{H}_5\text{HSO}_4$, is first formed and then

decomposes : (1) $C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$. (2) $C_2H_5HSO_4 = H_2SO_4 + C_2H_4$. This method of preparation appears to have been discovered by Becher (1669), but is first described by the Dutch chemists Deiman, Bondt, Lauwerenburgh, and Paets van Troostwijk in 1795. Ethylene was first clearly distinguished from methane by Dalton and by Henry in 1805.

30 ml. of alcohol and 80 ml. of concentrated sulphuric acid are heated in a litre flask at 160 - 170°, and a mixture of equal volumes of alcohol and sulphuric acid dropped in from a tap-funnel. The gas is washed with water and sodium hydroxide solution to remove carbon dioxide and sulphur dioxide. The ethylene is collected over water (Fig. 316).

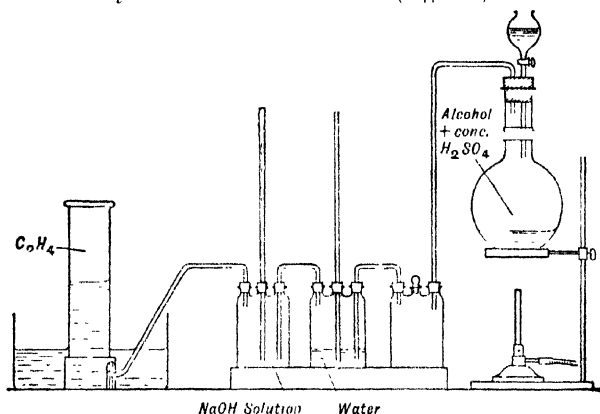
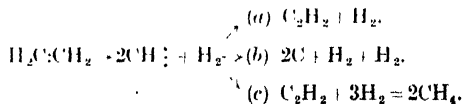


FIG. 316. Preparation of ethylene.

According to Newth's method (1901), alcohol is dropped by a tube reaching to the bottom of a distilling flask into 50 ml. of syrupy phosphoric acid which has been boiled till the temperature rises to 200°-220°; or alcohol vapour from one flask is passed through phosphoric acid at 220° in a second flask. The gas is passed through a tube cooled in ice. This gives a very pure gas, which may be collected over saturated sodium sulphate solution.

Properties of ethylene.—Ethylene is a colourless gas with a peculiar sweet smell. It is slightly soluble in water and very soluble in alcohol. B. pt. -103.7°, m. pt. -169.5°; critical temperature 9.5°, critical pressure 50.65 atm. Pure ethylene has been used as an anaesthetic and for "ripening" fruit. On sparking, the gas is decomposed into carbon and hydrogen. When passed through a red-hot tube it gives hydrogen, acetylene, and methane, with deposition of a lustrous film of carbon.

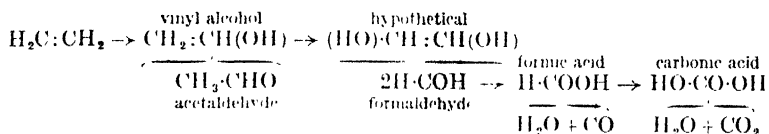
According to Bone and Coward, the thermal decomposition of ethylene may be represented by the following scheme :



The radical $\text{CH}_2\cdot$ is supposed to have a transient existence : it may undergo polymerisation, with formation of complex ring compounds.

Ethylene burns in air with a smoky luminous flame, but in oxygen the flame is very bright and does not smoke. When mixed with oxygen in the proportions of 1 : 3 by volume and kindled, ethylene explodes violently, and undergoes complete combustion : $\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$. If ethylene is mixed with an equal volume of oxygen and fired by a spark, expansion occurs and carbon monoxide and hydrogen are formed : $\text{C}_2\text{H}_4 + \text{O}_2 = 2\text{CO} + 2\text{H}_2$. If the resulting mixture, which burns with a blue flame in air, is mixed with half its bulk of oxygen and again exploded, carbon dioxide and steam are formed : $2\text{CO} + 2\text{H}_2 + 2\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$ (Dalton, 1810).

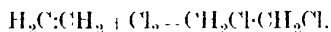
The combustion of ethylene is represented by Bone as follows :



The production of hydrogen in the incomplete explosive combustion of hydrocarbons is considered as due to the secondary thermal decomposition of the formaldehyde : $\text{H}\text{-COH} = \text{H}_2 + \text{CO}$, and the free carbon from decomposition of acetaldehyde : $\text{CH}_3\text{CHO} = \text{C} + 2\text{H}_2 + \text{CO}$.

A mixture of 1 vol. of ethylene and 2 vols of chlorine when kindled burns with a red flame, fumes of hydrochloric acid and a dense black cloud of soot being formed : $\text{C}_2\text{H}_4 + 2\text{Cl}_2 = 4\text{HCl} + 2\text{C}$.

If ethylene is mixed over water with an equal volume of chlorine and the mixture exposed to light, contraction occurs and oily drops collect on the surface of the water. These consist of **ethylene dichloride** $\text{C}_2\text{H}_4\text{Cl}_2$, or *Dutch liquid*, formed by the direct addition of chlorine to the double bond in the ethylene molecule :



On account of this reaction, ethylene was called *olefiant gas* (i.e. oil-forming gas) by Fourcroy. Ethylene dichloride was discovered by the Dutch chemists in 1795. If passed into bromine covered with a layer of water, ethylene forms a colourless pleasant-smelling liquid, *ethylene dibromide* $\text{C}_2\text{H}_4\text{Br}_2$ or $\text{CH}_2\text{Br}\text{-CH}_2\text{Br}$, similar to the dichloride.

Ethylene combines with iodine, hydrobromic acid, and hydriodic acid at 100° , but not with hydrochloric acid : $\text{CH}_2:\text{CH}_2 + \text{HBr} = \text{CH}_3\text{-CH}_2\text{Br}$. When mixed with hydrogen and passed over reduced nickel at $130^\circ\text{-}150^\circ$, it forms the saturated hydrocarbon ethane : $\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$, or $\text{CH}_2:\text{CH}_2 + \text{H}_2 = \text{CH}_3\text{-CH}_3$. Hypochlorous acid forms **glycol chlorohydrin** : $\text{CH}_2:\text{CH}_2 + \text{HOCl} = \text{CH}_2\text{OH}\text{-CH}_2\text{Cl}$. Cold dilute potassium permanganate solution is decolorised by ethylene, hydrated manganese dioxide is deposited and the ethylene is oxidised to glycol :



Concentrated sulphuric acid absorbs ethylene slowly on shaking at the ordinary temperature, rapidly at 160° - 170° , with the formation of *ethylsulphuric acid* or *sulphovinic acid* $C_2H_5 \cdot HSO_4$: $C_2H_4 + H \cdot HSO_4 = C_2H_5 \cdot HSO_4$. When this is boiled with water, alcohol is produced: $C_2H_5 \cdot HSO_4 + HOH = C_2H_5 \cdot OH + H_2SO_4$. Fuming sulphuric acid rapidly absorbs ethylene, a reaction used in gas analysis as an alternative to absorption by bromine water. *Ethionic acid* $C_2H_4 \cdot H_2S_2O_7$, and *carbhy sulphate* $C_2H_4 \cdot S_2O_6$, are formed.

Acetylene.—By the action of water on carbide of potassium formed in the preparation of the metal from potassium carbonate and charcoal (p. 698), Edmund Davy (1836) obtained a hydrocarbon, which was rediscovered by Berthelot in 1860 and called by him acetylene. He showed that it is formed when ethylene or alcohol



FIG. 317.-- Berthelot's synthesis of acetylene.

vapour is passed through a red-hot tube, and (in 1862) by direct synthesis from its elements when an electric arc burns between carbon poles in an atmosphere of hydrogen (Fig. 317): $2C + H_2 = C_2H_2$. Small quantities of methane and ethane are also formed by independent reactions.

Acetylene is formed when a Bunsen burner "strikes back," *i.e.* when the coal gas burns at the lower small jet, with a limited supply of air and in contact with the metal tube, which cools the flame. The peculiar smell noticed is said to be due to acetylene, although it may be due to formaldehyde. The acetylene is probably formed from the thermal decomposition of the ethylene in the coal gas.

The acetylene in the gas is detected by holding over the burner a globe wetted inside with ammoniacal cuprous chloride solution. The dark blue liquid is rapidly covered with a red film of cuprous acetylide Cu_2C_2 , which is explosive when dry.

Acetylene is prepared by the action of water on calcium carbide (Wöhler, 1862): $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$.

Cover the bottom of a conical flask with a layer of sand, and place on this a small heap of calcium carbide (Fig. 318). Displace the air with coal gas, and allow water to drop slowly on the carbide. Acetylene is rapidly evolved,

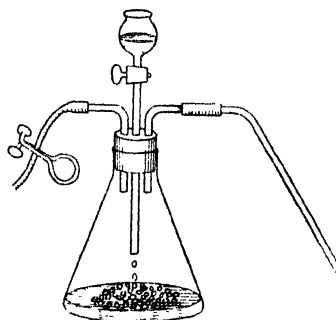


FIG. 318.--Preparation of acetylene

and will burn with a very luminous smoky flame. The acetylene prepared from commercial carbide has an unpleasant smell, due to impurities such as phosphine PH_3 , removed by passing through a solution of bleaching powder. Acetylene generators act on the principle of the Kipp apparatus, or else a regulated stream of water drops on the carbide.

Pure acetylene is evolved on decomposing cuprous acetylide with potassium cyanide solution: $\text{Cu}_2\text{Cl}_2 + 2\text{KCN} + 2\text{H}_2\text{O} \rightarrow 2\text{CuCN} + 2\text{KOH} + \text{C}_2\text{H}_2$; or when ethylene dibromide is dropped into boiling alcoholic potash (or sodium ethoxide dissolved in alcohol): $\text{CH}_2\text{Br}-\text{CH}_2\text{Br} + 2\text{KOH} \rightarrow \text{CH}::\text{CH} + 2\text{KBr} + 2\text{H}_2\text{O}$. The compound $\text{C}_2\text{H}_3\text{Br}$ is formed in an intermediate stage.

Properties of acetylene.—Acetylene is a colourless gas with an ethereal smell when pure, but when impure it has an unpleasant odour. When strongly cooled it forms a white solid subliming at -83.6° . Under 1.25 atm. pressure the solid melts at -81° to a colourless liquid. The critical temperature is 35.5° , the critical pressure 61.65 atm. The gas dissolves in its own volume of water at 15° and is more soluble in alcohol. Acetylene ignites at 428° in air, burning with a very smoky luminous flame, but if supplied to special burners under a pressure of 2–8 in. of water, so as to escape through fine capillaries and mix with a regulated amount of air, the flame is very bright and does not smoke.

Acetylene explodes with oxygen with extreme violence: $2\text{C}_2\text{H}_2 + 5\text{O}_2 = 4\text{CO}_2 + 2\text{H}_2\text{O}$; it is unsafe to try the experiment, as strong glass vessels are shattered by the explosion.

Mixtures of acetylene and air in proportions varying from 4 : 5 to 4 : 80, are explosive. Coal gas is explosive only when mixed with air within the limits 1 of gas to 5–13 of air, and the lower limit of explosion for methane is 5.4 per cent in air. The danger of explosion with acetylene is much greater than with coal gas.

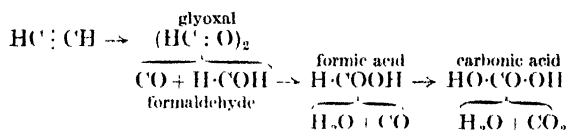
Acetylene forms with the haemoglobin of the blood a compound which, unlike that produced by carbon monoxide, is unstable and is readily decomposed by aeration. The pure gas has been used as an anaesthetic.

Acetylene is an endothermic compound: $2\text{C} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 - 47.8 \text{ k. cal.}$ It is unstable, and readily explodes under moderate pressure. It is therefore generated as required, or is absorbed in acetone, which dissolves 300 vols. of the gas under 12 atm. pressure. The acetone is soaked up in porous material ("kapok") contained in steel bottles. The chief use of acetylene is for illumination, and for the oxy-acetylene blowpipe, but it is finding increasing applications in the synthesis of organic compounds.

Acetylene is unsaturated and forms addition compounds. Chlorine explodes violently with the gas, but by passing the two gases alternately into sulphur chloride containing a little reduced iron, combination occurs to form acetylene dichloride $\text{CHCl}::\text{CHCl}$, and tetrachloride $\text{CHCl}_2::\text{CHCl}_2$. These are used as solvents. In contact with platinum black acetylene combines with two or four atoms of hydrogen, forming ethylene or ethane, C_2H_4 or C_2H_6 , respectively. Hydrobromic acid forms $\text{CH}_2::\text{CHBr}$ and $\text{CH}_3::\text{CHBr}_2$ (ethylidene bromide, isomeric with ethylene dibromide $\text{CH}_2\text{Br}::\text{CH}_2\text{Br}$).

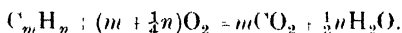
If acetylene is passed into a boiling solution of 3 vols. of sulphuric acid and 7 vols. of water to which a few per cent of mercuric sulphate is added, acetaldehyde $\text{CH}_3::\text{CHO}$ is formed and distils. From acetaldehyde, alcohol $\text{CH}_3::\text{CH}_2\text{OH}$, can be obtained by reduction; on oxidation, aldehyde forms acetic acid $\text{CH}_3::\text{COOH}$.

The combustion of acetylene is represented by Bone according to the scheme :



When acetylene is heated to dull redness, polymerisation occurs and a liquid mixture of hydrocarbons is obtained, one of which is benzene, $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$. This is an example of the conversion of an aliphatic into an aromatic hydrocarbon. A certain amount of the acetylene forms the free radical $\text{CH} \cdot$, which decomposes into carbon and hydrogen, the latter combining with the $\text{CH} \cdot$ to form methane CH_4 .

The composition of gaseous hydrocarbons.—When a measured volume of a gaseous hydrocarbon is mixed in a eudiometer with a measured excess of oxygen, and the mixture exploded by a spark, water and carbon dioxide are formed :



The water condenses to liquid on cooling and the carbon dioxide may be absorbed by potash solution and its volume found. The residual gas is the excess of oxygen used.

Since the volume of carbon dioxide is equal to the volume of oxygen used in burning the carbon, say m c.c., then if x c.c. of oxygen were originally taken and z c.c. remain unabsorbed after the experiment, it follows that the volume of oxygen used in the combustion of the hydrogen is $y = x - (m + z) = \frac{1}{2}n$ c.c. This volume of oxygen would correspond with a volume $2y$ or n of hydrogen existing in the free gaseous state. Each volume of carbon dioxide corresponds with one atom of carbon and each volume of hydrogen with two atoms of hydrogen. Thence the composition of the hydrocarbon is easily calculated.

The results are shown in a table. To avoid decimals, larger volumes of gas are specified than would conveniently be used, and the explosion of ethylene or acetylene with oxygen in a eudiometer is attended with danger.

Gas	Vol. taken	Vol. of oxygen added	Vol. after explosion	Contraction with vol. CO_2	Residual oxygen	Vol. of O_2 combg. with H_2	Vol. of hydrogen
Methane -	30 c.c.	66 c.c.	36 c.c.	30 c.c.	6 c.c.	30 c.c.	60 c.c.
Ethylene -	30 ..	95 ..	65 ..	60 ..	5 ..	30 ..	60 ..
Acetylene	10 ..	30 ..	25 ..	20 ..	5 ..	5 ..	10 ..

The table shows that 1 vol. of methane gives 1 vol. of carbon dioxide and contains an amount of hydrogen equivalent to 2 vols. in the free state. Thus, 1 molecule of methane contains 1 atom of carbon and 2 molecules or 4 atoms of hydrogen, and its formula is CH_4 . This is confirmed by the density. 1 vol. of ethylene gives 2 vols. of carbon dioxide and contains an amount of hydrogen equivalent to 2 vols. in the free state. Thus, 1 molecule of ethylene contains 2 atoms of carbon and 4 atoms of hydrogen, and the formula is C_2H_4 . 1 vol. of acetylene gives

2 vols. of carbon dioxide and contains an amount of hydrogen equivalent to 1 vol. in the free state. Thus, 1 molecule of ethylene contains 2 atoms of carbon and 2 atoms of hydrogen, and the formula is C_2H_2 .

Coal gas. The distillation of coal with the formation of gas was carried out by the Rev. John Clayton in 1688, the results being published in 1739. It was also described by Bishop Watson, who found that gas, tar, and a watery liquid were formed. The use of coal gas as an illuminant was introduced by William Murdock in 1792; in 1798 he installed a gas plant for lighting the factory of Boulton and Watt at Soho, near Birmingham. Gas lighting was introduced into Salford factories in 1805, the first public gas-works being erected there, and about the same time gas lighting was used on a very small scale in London, the streets of which were lighted by gas in 1808, Paris following in 1815. The use of gas in dwelling-houses came much later.

In the gas-works bituminous coal is "carbonised" in fire-clay *retorts* (Fig. 319) heated by producer gas formed by passing air and steam through incandescent coke. The gas evolved from the coal passes by way of vertical *ascension pipes* to a long horizontal *hydraulic main*, which serves as a water-seal, preventing gas passing back when a retort is opened. In the hydraulic main partial separation occurs into crude gas, ammoniacal liquor, and tar. The gas leaving the main at about 60° contains the following impurities, in per cent by volume, which are later removed:

Ammonia	-	0.7	1.4	Hydrogen sulphide	-	0.9	1.7
Hydrocyanic acid	-	0.05	0.15	Carbon disulphide	-	0.02	0.04

More tar is separated in the *condensers*, a series of air- or water-cooled iron pipes. Ammoniacal liquor deposits with the tar, and the two collect in the tar-well. The gas passes to *exhausters*, which maintain a slightly reduced pressure back to the retorts, and force the gas forwards to the purifiers and finally into the gas-holder. From the exhausters the gas passes to a *tar separator* in which tar fog is taken out, say by dividing the gas into fine streams which impinge on a solid surface to which the tar droplets adhere. The gas then passes to a *washer*, an iron tower packed with coke or wooden boards set on edge, down which water passes, which removes the rest of the ammonia.

The scrubbed gas contains as impurities: carbon dioxide, hydrogen sulphide (a portion of each gas is deposited with the ammonia in the previous cooling and scrubbing), and carbon disulphide. 100 cubic feet of crude gas contain upwards of 400 grains of sulphur as H_2S and 40 grains as CS_2 . It passes to the *purifiers*, in which it passes over trays covered with hydrated ferric oxide ("bog iron ore"). The oxide of iron decomposes the hydrogen sulphide with formation of ferric sulphide: $2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$. The oxide is "revivified" by exposure to air, when sulphur is separated and hydrated ferric oxide regenerated: $2Fe_2S_3 + 3O_2 + 6H_2O = 4Fe(OH)_3 + 6S$. The old method of removing carbon disulphide was to pass the gas through slaked lime previously used to remove hydrogen sulphide: $Ca(OH)_2 + 2H_2S = Ca(HS)_2 + 2H_2O$ ("foul lime"), when a thiocarbonate is formed: $Ca(HS)_2 + CS_2 = CaCS_3 + H_2S$. The hydrogen sulphide evolved is re-

moved in a second purifier. The carbon disulphide is now often left in the gas; it may be removed by a catalytic process in which the

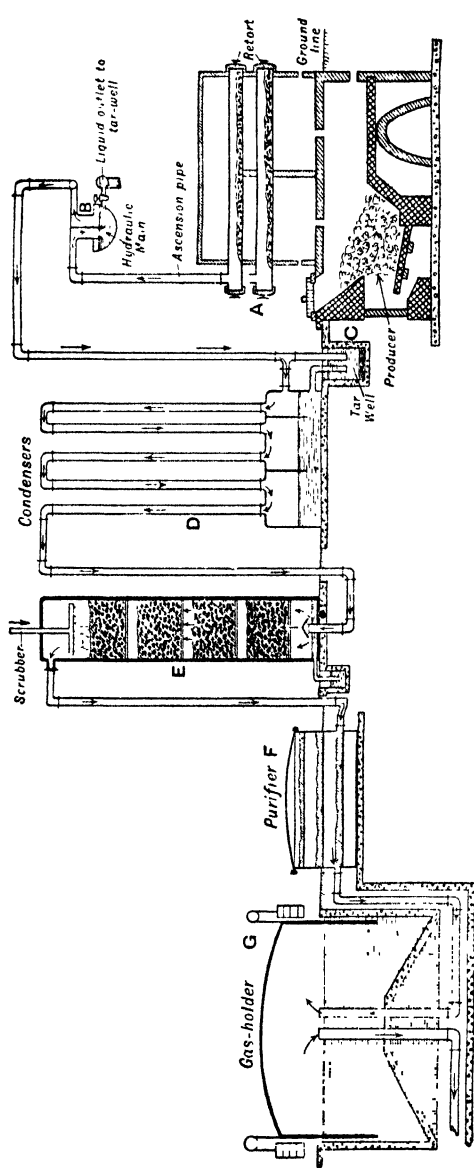


Fig. 319. Coal-gas manufacture (diagrammatic).

On the right two banks of horizontal fire-clay retorts *A* are shown in section. They are fitted with doors at each end to facilitate removal of the coke, and are heated to about 700° by gas made in the gas-producer shown below. The crude gas from the retorts passes to the hydraulic main, shown in cross-section at *B*, in which it is cooled to about 60° , and the liquid which separates passes to the tar-well *C*. The gas then passes through the air- or water-cooled pipes of the condensers *D*, in which it is cooled to atmospheric temperature and as a result more tar and ammoniacal liquor are separated and pass into the tar-well. After passing through exhausters and a tar-separator (not shown in the figure) the gas passes through washers or scrubbers *E*, the type shown being an iron tower containing coke packed in sections, over which a stream of water is passed downwards, the gas passing upwards. The washed gas then passes through the purifiers *F*, containing hydrated ferric oxide, in which the hydrogen sulphide is removed. The purified gas then passes into the gas-holder *G*, the one shown being of the wet type and drawn on a much smaller scale than the rest of the apparatus.

gas is passed over nickel at 450° : $\text{CS}_2 + 2\text{H}_2 = 2\text{H}_2\text{S} + \text{C}$. The hydrogen sulphide formed is removed as usual.

The purified gas passes to the *gas-holder*, a counterpoised iron bell sealed below by water, or an iron tower with a piston sealed by flowing tar. The purified gas should contain less than 1 part of H_2S per 10,000,000 parts, *i.e.* it should not blacken lead acetate paper in less than 3 minutes.

Cyanides (which are of value) are removed from the crude gas by passing through a washer containing ferrous sulphate and alkali, when ferrocyanide is produced; or through ammoniacal liquor containing ammonium sulphide with powdered sulphur in suspension, when a solution of ammonium thiocyanate is formed: $(NH_4)_2S_2 + NH_4CN \rightarrow (NH_4)_2S + NH_4CNS$.

The average composition of genuine coal gas, in percentages by volume, is as follows:

Hydrogen	-	-	-	-	-	38	-55	} <i>Diluents</i> , non-illuminating, but heat-producing.
Methane	-	-	-	-	-	22	-25	
Carbon monoxide	-	-	-	-	-	4	15	
Olefins, acetylene and benzene	-	-	-	-	-	2.5	5	} <i>Illuminants</i> , unsaturated hydrocarbons.
Nitrogen (mostly from air leakage)	-	-	-	-	-	2	-20	
Carbon dioxide	-	-	-	-	-	0	-3	} <i>Inerts</i> .
Oxygen	-	-	-	-	-	0	1.5	

The calorific value of coal gas is about 450 to 560 B.Th.U. per cu. ft. gross. Modern gas is often mixed with water gas, produced by blowing steam over red-hot coke: $C + H_2O \rightleftharpoons CO + H_2$. In this way the percentage of carbon monoxide is increased and that of methane diminished. Carbonisation in large vertical retorts of silica brick is now much used, more or less steam being introduced into the retort, and the coke extracted continuously below and coal fed in at the top. In many works, the gas after purification is dehydrated before it enters the holder by scrubbing with concentrated calcium chloride solution, and to prevent subsequent re-wetting of the gas, the water in the holder is covered with a film of suitable oil.

The hydrogen is probably derived from the decomposition (at 800° – 1000°) of gaseous hydrocarbons in contact with the red-hot walls of the retort. The carbon formed deposits as a hard greyish-black mass of *gas carbon*, which is removed by chipping. This is a pure form of carbon, density 2.35, which is a good conductor of electricity and is used for the pencils of arc lamps or in electric batteries.

According to Hofmann and Röehling it is a mixture of graphite with a very hard variety of carbon, which they call *lustrous carbon*, silvery in appearance, density 2.07, which is a moderately good conductor of electricity and is deposited on a glazed porcelain surface at 800° – 1000° from gas containing methane, in the form of a brilliant layer. It is chemically very inert, resisting nitric acid and even fused sodium sulphate.

The luminosity of coal gas flames is due entirely to olefin hydrocarbons *e.g.* ethylene (about 3 per cent), acetylene (0.06–0.07 per cent), and benzene vapour.

The effect of such hydrocarbons on the luminosity of flames may be illustrated by fitting a brass jet to each arm of a Y-tube, in one arm of

which is a piece of cotton wool soaked in toluene (Fig. 320), attaching the tube to a hydrogen apparatus, and lighting the two jets, after the air is displaced from the apparatus. The hydrogen saturated with toluene vapour burns with a luminous flame.

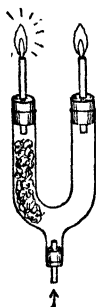
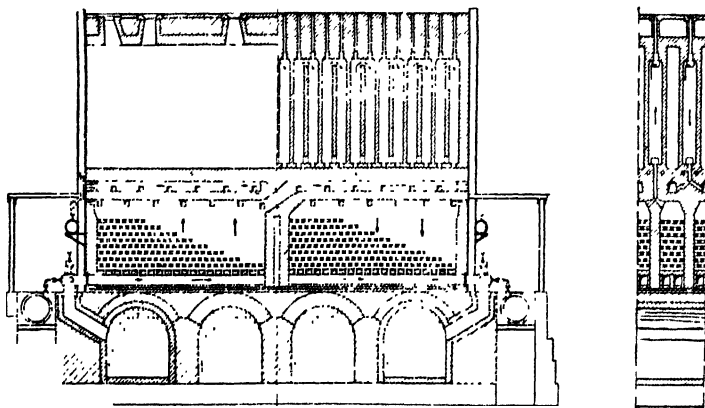


FIG. 320.—Luminosity imparted to hydrogen flame.

Coke.—The red-hot residue in the gas retorts is raked out, or pushed out by rams, through doors opened at the front and back, and quenched with water. It is known as gas coke, and used as fuel. It is greyish-black, porous, and brittle, and contains all the ash of the coal, about half the sulphur, and small quantities of nitrogen, hydrogen, and oxygen. The average percentage of carbon is 81.

The yields from 1 ton of Newcastle coal in gas-making are: 12,500 cu. ft. of gas; 1 gallon of light oil scrubbed from the gas; 110 lb. of tar, yielding 77 lb. of pitch; 7 lb. of ammonia; and 65–70 per cent of the weight of the coal as coke.

A hard variety of coke for metallurgical purposes (*e.g.* blast furnaces) is prepared by carbonising coal in *coke-ovens*. The old “beehive” oven consists of a covered mound of brickwork, in which the coal is partly burnt in a limited supply of air, as in charcoal burning. The high temperature produced carbonises the rest of the coal, and all the volatile



Courtesy of 'Coke Oven Managers' Association and Dr. R. A. Mott.
FIG. 321.—Koppers coke-oven with “hair-pin” circulation flues and cross-over regenerator.

products are lost. In modern “recovery ovens,” *e.g.* the Otto, Simon-Carvès or Koppers ovens, the coal is heated in closed fireclay or silica-brick retorts, 40 ft. long, 14–18 in. wide and 12 ft. 6 in. high (Fig. 321), by flues passing between them in which part of the gas evolved, mixed with air preheated in regenerators (*cf.* p. 920), is burnt. The gas from

the ovens is cooled to separate tar and scrubbed with creosote or other oil to recover benzene. The coke is pushed out by rams and quenched with water. On account of the value of the tar, gas, benzene, and ammonia, the use of recovery ovens has replaced the old beehive oven.

If powdered petroleum coke, gas (retort) carbon, or anthracite, is mixed with soot and pitch or tar-oil, is moulded and strongly heated in closed retorts, a compact variety of carbon which is a good conductor of electricity is obtained. This process is used in the manufacture of *carbon electrodes* for electric furnaces and arc lamps.

“Low temperature carbonisation” aims at treating bituminous coal at a temperature of 425°–760° C. instead of 1000° as in ordinary gas works or coke oven treatment. A ton of coal then gives about 14 cwt. of smokeless free burning fuel, together with 1½ gallons of crude light oil, 15–20 gallons of tar (which is different in composition from high temperature tar) and 3500–6000 cu. ft. of gas of calorific value 650–800 B.Th.U. per cu. ft.

Crude benzene (“benzol”) is now usually extracted from coal gas or coke-oven gas by washing with a suitable oil, or by adsorption in charcoal, and is recovered. This reduces the carbon disulphide and sulphur compounds in the gas by half, and also takes out about 95 per cent of the naphthalene. The naphthalene in gas tends to be deposited as a solid in pipes, causing stoppages.

CHAPTER XXXIII

OXYGEN COMPOUNDS OF CARBON. FLAME

The oxides of carbon.—Three oxides of carbon gaseous at the ordinary temperature are known :

Carbon dioxide CO_2 , colourless gas, b.pt. -56° at 5.3 atm. pressure, sublimation temperature -78.52° , critical temperature 31.1° , critical pressure 72.85 atm. ; the anhydride of carbonic acid $\text{HO}\cdot\text{CO}\cdot\text{OH}$ (known only in solution).

Carbon monoxide CO , colourless gas, b.pt. -191.5° , m.pt. -200° , critical temperature -138.7° , critical pressure 34.6 atm. ; the anhydride of formic acid $\text{H}\cdot\text{CO}\cdot\text{OH}$.

Carbon suboxide C_3O_2 , colourless gas, b.pt. $+6^\circ$, m.pt. -111.3° , the (double) anhydride of malonic acid $\text{CH}_2(\text{COOH})_2$.

The solid oxides C_4O_3 , C_6O_3 , and C_{12}O_9 have also been described, and salts of the percarbonic acids $\text{H}_2\text{C}'\text{O}_4$ and $\text{H}_2\text{C}'_2\text{O}_6$ are known.

CARBON DIOXIDE.

Carbon dioxide was first prepared by Van Helmont about 1630 ; he called it *gas sylvestre*. It was examined by Joseph Black (1755), and more fully by Bergman (1774), and was clearly recognised as an oxide of carbon by Lavoisier (1783). Lavoisier determined its composition by burning charcoal and diamond in oxygen, showed that it combines with bases to form salts (as had been discovered by Black), and called it *acide carbonique*. It was long known as "carbonic acid gas."

Carbon dioxide issues in abundance from the earth in the Poison Valley (Java) and the Grotto del Cane (Naples), and the gas from such sources, as well as that collecting in cellars (which extinguishes a candle) is mentioned by Pliny. It occurs in many mineral waters, such as those of Selters, Vichy, and the Geyser Spring of Saratoga. By the combustion of coal and other carbonaceous fuels, and other processes (p. 627), large quantities of it pass into the atmosphere, which contains about 3 vols. of CO_2 in 10,000. Carbon dioxide is formed during *respiration*, as may be shown by blowing expired air through lime-water, which becomes milky. Carbon dioxide is evolved in the *fermentation* of sugar in the preparation of beer and wine : $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_2\text{H}_5\text{OH}$ (*alcohol*) + 2CO_2 , and in other kinds of fermentation and the decay of organic matter.

Large quantities of carbon dioxide produced by combustion (p. 620) or from marble and acid are liquefied by compression. The liquid is sold in large steel cylinders, from which gas may be taken by standing the cylinder upright with the valve above. If the cylinder is laid on its

side and the valve opened, a jet of liquid carbon dioxide issues, which at once freezes to a snow-like solid. This may be collected in a canvas bag tied to the valve. The solid may be handled with a horn spoon; if pressed between the fingers it produces painful blisters. It is sold in compact blocks as "dry ice," or "drikold," for use in refrigeration, and for producing the gas.

The boiling point of carbon dioxide is -56° under 5.3 atm. pressure. The liquid cannot exist under atmospheric pressure. The sublimation point of the solid at atmospheric pressure is -78.5° ; a mixture of solid carbon dioxide and ether is a convenient cooling agent and may be contained in a Dewar cylinder.

Cut a circular groove in a large cork, and fill it with mercury. Place over the whole a mixture of solid carbon dioxide and ether, by means of a horn spoon. The mercury rapidly freezes. Knock out the ring of solid mercury, and suspend it by a glass hook in a jar of water. A ring of ice is formed, and the mercury melts.

If solid carbon dioxide is sealed up in a strong glass tube, it melts under pressure to a liquid. If the tube is warmed gently, the liquid expands very rapidly, and at 31° the meniscus disappears. At the same instant the tube is filled with a flickering fog, which at once vanishes. On cooling, the reverse changes occur: 31° is the critical temperature of carbon dioxide.

Preparation of carbon dioxide.—Carbon dioxide is prepared in the laboratory by the action of acids on carbonates: $2\text{H}^+ + \text{CO}_3^{=} = \text{CO}_2 + \text{H}_2\text{O}$.

Pieces of marble and dilute hydrochloric acid in a Woulfe's bottle or Kipp's apparatus are generally used: $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$. The gas is washed with a little water, or passed through a solution of sodium bicarbonate to eliminate acid spray, and is collected by downward displacement, since it is 1.53 times as heavy as air. The gas may be dried by calcium chloride, sulphuric acid or phosphorus pentoxide. The gas usually contains a little air unless the pieces of marble are boiled for some time with water before use.

If *dilute* sulphuric acid is added, marble soon becomes coated with sparingly soluble calcium sulphate, and action ceases. If finely-powdered chalk is used, the reaction is complete, but frothing occurs. Marble or chalk dissolves readily in concentrated sulphuric acid if a little water is added, since the calcium sulphate forms a soluble acid sulphate, $\text{CaH}_2(\text{SO}_4)_2$. To remove sulphur dioxide, a common impurity, the gas is passed through potassium permanganate solution.

Pure carbon dioxide is obtained by heating pure sodium bicarbonate: $2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$; by the action of dilute sulphuric acid (boiled to free it from air) on pure sodium carbonate: $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$; or by heating a mixture of 1 part of sodium carbonate with 3 parts of potassium dichromate: $\text{Na}_2\text{CO}_3 + \text{K}_2\text{Cr}_2\text{O}_7 = \text{Na}_2\text{CrO}_4 + \text{K}_2\text{CrO}_4 + \text{CO}_2$.

Carbon dioxide is evolved on heating all carbonates except the normal carbonates of the alkali metals and barium carbonate: chalk,

limestone, marble, *magnesia alba*, etc., evolve carbon dioxide at a red heat: $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$.

An impure gas, mixed with nitrogen, is formed by passing a slight excess of air over red-hot coke or charcoal: $\text{C} + \text{O}_2 = \text{CO}_2$. If this gas is passed into concentrated potassium carbonate solution, the carbon dioxide is absorbed to form potassium bicarbonate. On heating the solution, pure carbon dioxide, free from nitrogen, is evolved, leaving a solution of potassium carbonate which is used again: $\text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{KHCO}_3$.

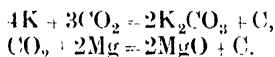
Properties of carbon dioxide.—Carbon dioxide is a colourless gas with a faint pungent smell and a slight acid taste. It extinguishes a burning taper, sulphur, phosphorus, etc.; air in which a taper has burnt out contains $2\frac{1}{2}$ per cent by volume of carbon dioxide and $17\frac{1}{2}$ per cent of oxygen is still present. The gas is used in extinguishing fires.

Ignite a little benzeno in a porcelain dish, and decant over it a large bell-jar of carbon dioxide. The flame is extinguished.

Fire extinguishers consist of a strong metal vessel containing a solution of sodium carbonate, with a glass tube or bottle of sulphuric acid inside. By means of a rod attached to a knob outside the glass tube may be broken, or by inverting the container the acid poured from the bottle, and the mixture of liquid and gas then issues forcibly from the nozzle.

Carbon dioxide does not support respiration, and animals die in it from suffocation, but it is not poisonous and if oxygen is taken in time recovery with no ill-effect follows.

Burning sodium, potassium, and magnesium continue to burn in carbon dioxide, with separation of pure carbon:



Burn a piece of magnesium ribbon (or stout wire) in a jar of dry carbon dioxide. Treat the residue with dilute sulphuric acid; magnesia dissolves and black specks of carbon float in the liquid.

A mixture of solid carbon dioxide and magnesium powder burns with a brilliant flash when kindled, leaving magnesia and carbon. A piece of sodium heated in carbon dioxide in a test-tube forms carbon monoxide: $2\text{Na} + 2\text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{CO}$. Potassium forms some potassium oxalate: $2\text{K} + 2\text{CO}_2 = \text{K}_2\text{C}_2\text{O}_4$.

A characteristic reaction of carbon dioxide is the formation of a white precipitate of calcium or barium carbonate when the gas is passed into, or shaken with, lime-water or baryta-water: $\text{Ca}(\text{OH})_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$.

At high temperatures carbon dioxide dissociates into carbon monoxide and oxygen: $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$; at different temperatures at atmospheric pressure the percentage dissociations are:

Temperature abs.	-	1000°	1500°	2000°	2500°	3000°	3500°
% dissociation	-	0.00025	0.0483	2.05	17.6	54.8	83.2

Deville (1865) found that if a rapid stream of carbon dioxide was passed through a porcelain tube heated to about 1300°, and the issuing

gas collected over potassium hydroxide solution (which absorbs carbon dioxide), a small amount of a mixture of carbon monoxide and oxygen was obtained, indicating a dissociation of about 0.2 per cent. The gas is also decomposed by electric sparks, and at 3-5 mm. pressure 65-70 per cent is decomposed by a silent discharge.

The composition of carbon dioxide.—The composition of carbon dioxide may be found by weight and by volume. The composition by weight is determined by burning a weighed amount of pure carbon in oxygen, and weighing the carbon dioxide, usually after absorption.

About 1 gm. of purified sugar-charcoal is weighed into a porcelain boat *X*, placed inside a hard glass tube *Y*, one half of which is packed with recently-ignited granular copper oxide *Z* (Fig. 322). The purifying apparatus, consisting of U-tubes *A* and *B* containing broken sticks of caustic potash, and the absorption apparatus consisting of the weighed potash-bulbs *C* containing concentrated potassium hydroxide solution, with a calcium chloride tube *D*, are attached as shown. The tube is laid in a combustion furnace. Sheets of asbestos are placed over the ends of the

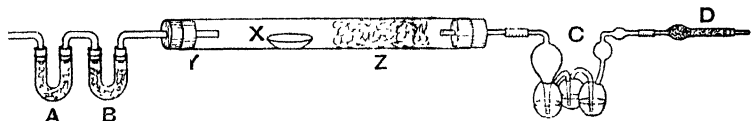


FIG. 322. Gravimetric composition of carbon dioxide.

tube, to protect the rubber stoppers from heat radiated from the furnace. The copper oxide is heated to redness, a *slow* stream of oxygen being passed. The burners under the boat are now lighted, and the combustion of the carbon carried out. The layer of hot copper oxide oxidises any carbon monoxide to carbon dioxide. The oxygen is allowed to pass after the combustion is finished to sweep out the carbon dioxide, then the oxygen is displaced by air. The potash-bulbs are detached, cooled and reweighed. The increase in weight represents the carbon dioxide formed. Let x = wt. of carbon, y = wt. of carbon dioxide; then $y - x$ = wt. of oxygen; \therefore carbon/oxygen in carbon dioxide = $x/(y - x)$.

Dumas and Stas (1841) carried out in this way five combustions of natural graphite, four of artificial graphite, and five of diamond. The results were in agreement, the mean weights of carbon combining with 800 parts of oxygen being as follows:

- 299.92 parts of natural graphite,
- 299.95 parts of artificial graphite,
- 300.02 parts of diamond.

Due allowance was made for ash remaining in the boat after the combustion.

The equivalent of carbon ($O = 8$) is thus almost exactly 3 and the atomic weight $3 \times 4 = 12$. The older results from the gravimetric synthesis of carbon dioxide were corrected by Scott for the expansion of the potash solution after absorption of carbon dioxide, which alters the air displacement. The physical method of limiting density (p. 105), gave 12.003

(Leduc ; Rayleigh ; CO) ; 12.007 (Moles and Salazar ; CO) ; and 12.0039 (Baume and Perrot ; CH₄). Owing to the existence of the isotope C = 13, the value is probably closer to 12.01 than to 12.00, and a value close to 12.01 was obtained by Whytlaw-Gray and Woodhead (1933) from the limiting density of carbon monoxide.

The volumetric composition of carbon dioxide is found, approximately, in the same apparatus as was used in the case of sulphur dioxide (p. 464). A piece of dry charcoal is burnt in a confined volume of dry oxygen over mercury. After cooling, the volume of gas is practically unchanged. Thus, the number of molecules of carbon dioxide produced is equal to the number of molecules of oxygen disappearing, or one molecule of carbon dioxide contains one molecule of oxygen. The density of carbon dioxide gives a molecular weight 44. This contains a molecular weight of oxygen, 32, so that the difference, 12, represents the carbon. A molecular weight of any volatile carbon compound never contains a smaller amount of carbon than 12 parts, so that 12 is the atomic weight of carbon, and the formula of carbon dioxide is CO₂.

Carbonic acid.—Carbon dioxide is fairly soluble in water, which at 15° dissolves about its own volume of the gas. Under pressures greater than 4–5 atm. at the ordinary temperature, the solubility increases at a slower rate than the pressure (*i.e.* according to Henry's law). On lowering the pressure the gas escapes with effervescence, although the liquid remains supersaturated and evolves gas slowly for some time. If the liquid is stirred, or if porous solids such as sugar or bread-crumbs are thrown into it, brisk effervescence results. The whole of the carbon dioxide dissolved is expelled on boiling. Aerated waters (*e.g.* *soda-water*) are charged with carbon dioxide under pressure ; "sparklets" are small iron bulbs containing liquid carbon dioxide. The gas is more soluble in alcohol than in water.

The solution of carbon dioxide has a faintly acid taste, and turns litmus a port wine red colour. If the amount of dissolved gas is increased by pressure, the litmus turns bright red. On boiling, carbon dioxide escapes and the blue colour is restored. A portion of dissolved gas seems to be combined with water to form carbonic acid H₂CO₃, and the solution shows very feeble acid properties, about one-fifth the strength of acetic acid (which displaces carbon dioxide from carbonates). Carbonic acid obeys Ostwald's dilution law, and the dissociation constants have been given as :

$$\begin{aligned} [\text{H}^+] \times [\text{HCO}_3'] / [\text{H}_2\text{CO}_3] &= 3.04 \times 10^{-7} \text{ at } 18^\circ \\ [\text{H}^+] \times [\text{CO}_3''] / [\text{HCO}_3'] &= 6.4 \times 10^{-11} \text{ at } 25^\circ. \end{aligned}$$

From theoretical considerations carbonic acid would be expected to be stronger than formic acid, H·CO·OH, since addition of a hydroxyl group, forming HO·CO·OH, should increase the acidic properties. The neutralisation of carbonic acid by alkali, with phenolphthalein as indicator, is not instantaneous as in ionic reactions, so that it is assumed that less than 1 per cent of the carbon dioxide is hydrated. The hydration reaction : CO₂ + H₂O ⇌ H₂CO₃, requires time. If the hydrogen ions in the solution are

referred, not to the total CO_2 (as above) but to the hydrated part H_2CO_3 , carbonic acid is found to be twice as strong as formic acid.

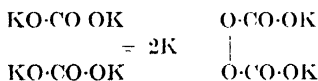
Since it dissociates in two stages, carbonic acid is dibasic and forms two series of salts :

1. Acid carbonates, *e.g.* NaHCO_3 , $\text{Ca}(\text{HCO}_3)_2$,
2. Normal carbonates, *e.g.* Na_2CO_3 , CaCO_3 .

The structural formula of the acid is written $\text{HO}\cdot\text{CO}\cdot\text{OH}$; esters of a hypothetical orthocarbonic acid, $\text{C}(\text{OH})_4$, *e.g.* ethyl orthocarbonate, $\text{C}(\text{OC}_2\text{H}_5)_4$, are known. A crystalline hydrate $\text{CO}_2\cdot 6\text{H}_2\text{O}$ is obtained under pressure at low temperatures.

The normal carbonates of alkali metals are hydrolysed in solution, and have an alkaline reaction : $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{NaHCO}_3$. A decinormal solution of sodium carbonate is 3.17 per cent hydrolysed at 25° .

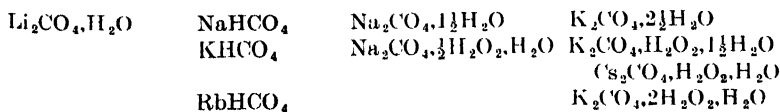
Percarbonates.—If a saturated solution of potassium carbonate is electrolysed at -10° to -15° , with a platinum anode enclosed in a porous cell, a bluish-white amorphous precipitate of potassium percarbonate $\text{K}_2\text{C}_2\text{O}_6$ deposits at the anode. This may be washed rapidly with cold water, alcohol, and ether, and dried over P_2O_5 . The formation of the salt is represented as follows :



It is fairly stable at the ordinary temperature when dry, but is decomposed by water with evolution of oxygen. The sodium salt can be prepared in solution by electrolysis at 0° of a solution of 60 gm. of sodium carbonate per litre. The electrolytic percarbonates liberate iodine immediately from cold potassium iodide solution : $\text{C}_2\text{O}_6'' + 2\text{I}' = 2\text{CO}_3'' + \text{I}_2$. These compounds are α -perdicarbonates derived from α -perdicarbonic acid $\text{HO}\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{OH}$.

Several other percarbonates are formed by chemical processes : (i) the action of hydrogen peroxide on concentrated solutions of alkali carbonates and precipitating the percarbonate with alcohol ; (ii) the action of hydrogen peroxide on a hydrated alkali peroxide at low temperature, or on an alkali ethoxide such as KOC_2H_5 . Compounds so prepared are β -perdicarbonates such as $\text{Na}_2\text{C}_2\text{O}_6$ and $\text{K}_2\text{C}_2\text{O}_6$, isomeric with the compounds prepared by electrolysis but with different properties ; and permonocarbonates derived from permonocarbonic acid H_2CO_4 . Some of these liberate iodine and oxygen gas from neutral concentrated potassium iodide solution, whilst others liberate only oxygen gas. The β -perdicarbonates may be derived from β -perdicarbonic acid $\text{HO}\cdot\text{O}\cdot\text{C}\cdot\text{O}\cdot\text{O}\cdot\text{C}\cdot\text{O}\cdot\text{OH}$, and the permonocarbonates from permonocarbonic acid $\text{HO}\cdot\text{O}\cdot\text{C}\cdot\text{O}\cdot\text{OH}$. The acids are unknown.

Some of the permonocarbonates contain water of crystallisation and some contain also hydrogen peroxide of crystallisation :



The percarbonates have been proposed as bleaching and disinfecting agents but they are not very stable as compared with perborates (p. 658).

The carbon dioxide cycle.—In very remote geological periods the atmosphere of the earth was probably very rich in carbon dioxide, whilst the primary rocks such as felspar, $K_2O, Al_2O_3, 6SiO_2$, consisted almost entirely of bases in combination with silica. At high temperatures, silica displaces carbon dioxide from carbonates, forming silicates. As the temperature fell, carbon dioxide and water in the atmosphere began to decompose the silicates with the formation of free silica (quartz), aluminium silicates (clay), soluble alkali carbonates, and bicarbonates of alkaline earths (e.g. potassium carbonate and calcium bicarbonate): $K_2O, Al_2O_3, 6SiO_2 + CO_2 + 2H_2O = K_2CO_3 + Al_2O_3, 2SiO_2, 2H_2O + 4SiO_2$. The soluble carbonates (e.g. K_2CO_3) were partly retained in the soil and were partly washed away to the sea.

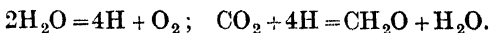
Meanwhile the water of the sea had come into equilibrium with the atmospheric carbon dioxide and dissolved some of it. The calcium and magnesium bicarbonates were used by marine organisms, which retained the normal carbonates and set free half the carbon dioxide, which was again evolved to the atmosphere. When the organisms died, the calcium carbonate of their shells deposited in the form of chalk beds or coral reefs (a process still going on), producing sedimentary rocks. In this way carbon dioxide was largely removed from the atmosphere and stored in the sedimentary rocks. It is estimated that 30,000 times as much carbon dioxide is contained in rocks as exists free in the atmosphere.

The carbon dioxide in the atmosphere was thus considerably reduced and more was taken out by the action of green plants in sunlight. The remains of these early plants form coal deposits.

Photosynthesis.—Green plants contain the pigment *chlorophyll*, associated with protoplasm in the form of corpuscles (*chloroplasts*) which are active during the absorption of atmospheric carbon dioxide by plants exposed to light.

In the leaves of green plants are special organs through which atmospheric water vapour, oxygen, a little nitrogen, and carbon dioxide in solution pass into the cell sap. In aquatic plants the gases are absorbed entirely from solution. Carbon dioxide is absorbed by all parts of the surface of the plant which contain chlorophyll, but mainly by the leaves, and it supplies the material from which the plant tissues are built. It is converted under the action of light into *carbohydrates*, such as sugars, having the empirical formula $(CH_2O)_x$.

By using an isotope of oxygen ^{18}O as a "tracer element" it has been shown that the oxygen evolved in photosynthesis comes from water, the nascent hydrogen from the water then reducing carbon dioxide to substances from which carbohydrates are ultimately produced:



The first product of photosynthesis is probably not formaldehyde, $H.COH$, as was formerly supposed, but appears to be an organic acid containing the $-COOH$ group.

By using isotopes of oxygen and carbon as "tracer elements" it has been shown that the oxygen evolved in photosynthesis comes from water and not carbon dioxide, the nascent hydrogen from the water then reducing the carbon dioxide to substances from which carbohydrates are produced.

The production of oxygen by the agency of living green plants under the influence of light was observed by Priestley, Ingen-Housz and Senebier, at the close of the eighteenth century.

Watercress, mint, or the common pond-weed *Elodea Canadensis*, is put into a flask filled with tap water and provided with an arrangement for collecting gas. On exposure to bright sunlight if available, otherwise to bright daylight, bubbles of gas are produced on the leaves, which rise into the test-tube (Fig. 323). These consist largely of *oxygen*. The water may first be saturated with carbon dioxide.

The influence of light in promoting chemical changes was met with also in the union of hydrogen and chlorine. In some cases the invisible ultra-violet rays of the spectrum are most active, and the violet end of the spectrum is often more chemically active than the red or intermediate parts. Nevertheless, the name *actinic rays*, formerly given to the violet and ultra-violet parts of the spectrum, is inappropriate, since *all* the rays of the spectrum may be chemically active in different reactions.

The formation of oxygen by the chlorophyll of plants occurs most rapidly in red and yellow light, which are absorbed by the green chlorophyll. This part of the spectrum corresponds with the position of maximum energy for high sun, or the wave-length 666 μ .

Hydrogen sulphide is most rapidly decomposed by *red* light, and in some cases even infra-red rays (so-called "heat rays") are most active. Light may also *retard* a chemical reaction: *e.g.* the oxidation of alkaline pyrogallol is retarded by violet light, but accelerated by red light.

The oxygen also absorbed by the plant from the atmosphere furnishes nearly all the energy by which its ordinary life processes are carried on, the light energy being concerned only with the photosynthesis. In the dark, only carbon dioxide is evolved by the leaves, but in light oxygen is evolved, although the smaller evolution of carbon dioxide continues.

The growth of plants.—The food of plants is entirely inorganic. Besides gases, plants require mineral matters, which are absorbed in solution from the soil by the roots. These include combined nitrogen as potassium chloride or sulphate, or the crude potash minerals of Stassfurt. Combined nitrogen is supplied in the form of Chile nitre, calcium nitrate, ammonium sulphate, blood, guano, and other nitrogenous animal products, and farmyard manure. It is in all cases converted into nitrates by micro-organisms in the soil before assimilation. Phos-



FIG. 323.—Production of oxygen by green plants in light.

phates are supplied as soluble superphosphate of lime, basic slag, bones, or other phosphates which can be dissolved by the carbonic acid evolved by decaying vegetable matter (*humus*) in the soil.

Small quantities of iron, lithium, boron, manganese, etc., also required are taken from the soil. Absorption occurs by selective permeation of the dissolved salts through the membranes of the root-hairs. If plants are supplied with carbon dioxide, air, and light, and the roots are immersed in a solution containing the necessary elements, they continue to grow.

Respiration.—We now consider those processes which tend to increase atmospheric carbon dioxide. Early experimenters such as Mayow, Scheele, Priestley, and Lavoisier, knew of the similarity between combustion and respiration. Lavoisier pointed out that oxygen breathed into the lungs oxidises the carbonaceous materials of the blood, producing carbon dioxide which is breathed out, and that animal heat results from this chemical process of oxidation. Mayow in 1674 (p. 25) had suggested that the process we now call oxidation occurs in the tissues. The blood absorbs oxygen (which he called the nitro-aerial spirit) from the air taken into the lungs in respiration, and the arterial blood conveys this to the tissues. The process of oxidation in the tissues produces animal heat.

The blood contains red corpuscles composed of protoplasm with a colouring matter known as *haemoglobin*, containing iron. Haemoglobin absorbs oxygen, producing a bright red substance which exists in the blood of the arteries, passing from the lungs to the tissues. In the tissues the loosely-combined oxygen is absorbed and oxidation processes occur. These are the source of animal heat and energy, and one of the products is carbon dioxide, which remains in solution as carbonic acid or bicarbonates. The de-oxygenated blood has now a dark purple colour, and part of it passes back to the heart by the veins, to be pumped to the lungs for re-aeration.

The expansion and contraction of the lungs, by which respiration occurs, are brought about by movements of the diaphragm and the ribs, both of which are co-ordinated by a nervous centre in the lower part of the brain. This centre is stimulated by carbonic acid dissolved in arterial blood passing through it. The reaction of the blood is normally feebly alkaline (pH = 7.4). To maintain this constant within narrow limits is the function especially of the kidneys. The carbonic acid formed in the blood by processes of oxidation is removed in the lungs in the form of carbon dioxide, which is breathed out in the expired air.

In consequence of the daylight activities of plants, absorbing carbon dioxide from the atmosphere, giving out oxygen, and the respiration of plants and animals, absorbing oxygen and giving out carbon dioxide, a balance is maintained between the amounts of oxygen and carbon dioxide in atmospheric air.

Atmospheric carbon dioxide.—Normal outdoor air contains about 3 volumes of carbon dioxide per 10,000. The average figures for air at Kew are 2.43 (minimum)–3.60 (maximum). On Mont Blanc the figures are 2.62 at 1080 m., and 2.69 at 3050 m. In crowded towns and especially in rooms not sufficiently ventilated, the carbon dioxide may

rise to 0.04-0.3 per cent by volume. The continued breathing of air containing 0.2 per cent of CO_2 is injurious (Angus Smith). The "stiffness" of badly ventilated spaces is chiefly the effect of the water vapour from the lungs, which tends to saturate the stagnant air and impedes the evaporation of perspiration.

The total amount of carbon dioxide in the atmosphere corresponds with about 600,000 million tons of carbon. The sources of atmospheric carbon dioxide are respiration of animals and plants, combustion, fermentation, putrefaction, the soil (worms, decay, and gas of volcanic origin), mineral springs, volcanic activity, and lime-burning. Atmospheric carbon dioxide is diminished by absorption by the sea, photosynthesis by green plants, and the weathering of silicate rocks (1.62×10^9 tons of CO_2 per annum). On the whole, the carbon dioxide in the atmosphere seems to be slowly increasing, and slight changes of climate may be due partly to this cause.

In the determination of atmospheric carbon dioxide, a measured volume of air may be drawn by an aspirator first through a drying tube containing pumice soaked in sulphuric acid and then through a weighed tube containing soda-lime. This is followed by a tube of pumice and sulphuric acid to absorb moisture given off in the soda-lime tube, and the last two tubes are weighed together. A more convenient process is *Pettenkofer's method*. A measured volume of standard baryta water is shaken with a known volume of the air in a large (8-10 lit.) bottle, and the excess of baryta titrated with standard acid and phenolphthalein: $\text{Ba}(\text{OH})_2 \cdot \text{CO}_2 = \text{BaCO}_3 + \text{H}_2\text{O}$. Absorption is more rapid with a hot solution of baryta.

CARBON MONOXIDE

Lassone (1776) obtained an inflammable gas by heating charcoal with zinc oxide, and Priestley (1796) from charcoal and iron-scales (Fe_3O_4). Cruickshank (1800) found that the gas was not hydrogen, but an oxide of carbon containing less oxygen than carbon dioxide, and Clement and Desormes showed that it could be formed by passing carbon dioxide over red-hot charcoal. Dalton (1808) found that the gas requires half its volume of oxygen for combustion, and forms its own volume of carbon dioxide, so that formula is CO .

Carbon monoxide occurs in coal gas and in some volcanic gases. It is formed in the combustion of charcoal or coke in a limited supply of air; the blue flames seen on the top of a clear fire consist of burning carbon monoxide.

The presence of carbon monoxide in furnace gases is evidence of improper air supply, and its estimation in flue gases affords a check on the furnace efficiency. Poisoning by the fumes of burning charcoal, described by Hoffmann in 1716, is due to carbon monoxide, which is a dangerous poison. It is also formed in the combustion of petrol in automobile engines, the exhaust gases of which are very poisonous.

The production of carbon monoxide in a fire is usually supposed to be due to the reduction of the carbon dioxide, formed from the lower portions of the glowing fuel and the entering air, by passing through the

incandescent mass of carbon : $C + O_2 = CO_2$; $CO_2 + C = 2CO$. The monoxide burns on the top of the fire, where an excess of air is present. Dixon and Baker consider that carbon monoxide is a primary product in the combustion of carbon : $2C + O_2 = 2CO$. If carefully dried carbon is heated in oxygen dried by prolonged exposure to phosphorus pentoxide, principally carbon monoxide is formed, according to Baker. Wheeler found that both carbon monoxide and carbon dioxide are formed.

The reduction of carbon dioxide by carbon proceeds rather slowly below 800° , but above 1000° it is fairly rapid. The equilibrium : $C + CO_2 \rightleftharpoons 2CO$, is not usually reached in the combustion of carbon, and the composition of the resulting gas is variable. The table contains the *equilibrium* values at atmospheric pressure for various temperatures. The amount of carbon monoxide increases with the temperature.

Temperature	Per cent CO_2 by vol.	Per cent CO by vol.
850°	6.23	93.77
900°	2.22	97.78
950°	1.32	98.68
1000°	0.59	99.41
1050°	0.37	99.63
1100°	0.15	99.85
1200°	0.06	99.94

The formation of a *flame* of burning carbon monoxide when a diamond burns in air was noticed by Macquer in 1771 : large quantities of carbon monoxide are formed when a blast of air is forced through a layer of incandescent coke. The reverse reaction : $2CO = CO_2 + C$, was observed by Deville (1864) ; he found that carbon is deposited on a narrow silvered copper tube cooled by a stream of water and placed axially in a strongly-heated porcelain tube through which carbon dioxide was passed.

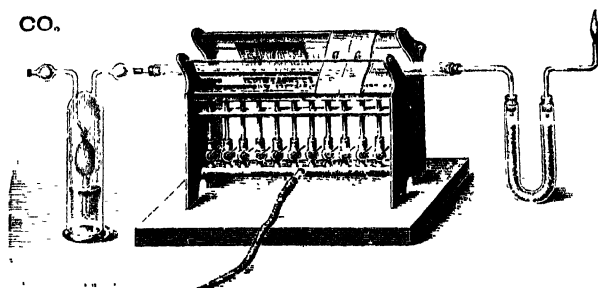


FIG. 324.—Carbon monoxide from carbon dioxide and carbon.

Pass a slow current of carbon dioxide over pieces of charcoal heated to bright redness in an iron tube (Fig. 324). The carbon dioxide is removed from the issuing gas by a tube of soda-lime, and the carbon monoxide may then be burnt at a jet.

Carbon monoxide is formed by heating charcoal with oxides of zinc, iron, or manganese : $C + ZnO = Zn + CO$, or with chalk or barium carbonate : $BaCO_3 + C = BaO + 2CO$, and by heating a mixture of calcium carbonate and zinc dust : $CaCO_3 + Zn = CaO + ZnO + CO$. It is also formed by passing carbon dioxide over zinc dust or iron filings heated to redness : $CO_2 + Zn = ZnO + CO$. Calcium, magnesium, and alkali-metals, cause the separation of free carbon : $2Ca + CO_2 = 2CaO + C$, and $4K + 3CO_2 = 2K_2CO_3 + C$.

Preparation of carbon monoxide.—Carbon monoxide is made on the large scale by passing carbon dioxide over heated carbon ; in the laboratory it is more conveniently prepared by heating formic acid (or sodium formate), oxalic acid, or potassium ferrocyanide, with concentrated sulphuric acid. These reactions were all discovered by Döbereiner about 1820.

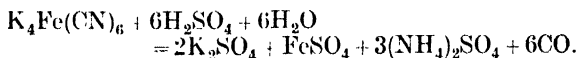
The gas from formic acid is very pure : $H \cdot COOH = H_2O + CO$; a trace of sulphur dioxide formed by reduction of the sulphuric acid : $H_2SO_4 + CO = CO_2 + SO_2 + H_2O$, is removed by washing with sodium hydroxide solution. A mixture of 85 parts of phosphorus pentoxide and 15 of water may be used with formic acid (Thompson, 1929).

Concentrated sulphuric acid is heated to 100° in a flask, and concentrated formic acid dropped in from a tap-funnel. Cold concentrated sulphuric acid may also be dropped on dry sodium formate in a flask. The gas may be dried with phosphorus pentoxide and collected over mercury. *Note : carbon monoxide is very poisonous.*

Oxalic acid crystals gently heated with concentrated sulphuric acid evolve a mixture of equal volumes of carbon monoxide and dioxide : $(COOH)_2 = CO + CO_2 + H_2O$. The carbon dioxide is removed by washing with alkali solution.

Twenty-five gm. of crystallised oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) are covered with concentrated sulphuric acid in a flask. On heating gently, brisk evolution of gas occurs. This is passed through a wash-bottle containing sodium hydroxide solution, and the carbon monoxide collected over water.

Potassium ferrocyanide crystals on heating with ten times the weight of concentrated sulphuric acid in a large flask evolve nearly pure carbon monoxide (except in the later stages of the reaction when sulphur dioxide is formed), but the reaction is violent :



The synthesis of formic acid is effected by the silent discharge : $CO + H_2O \rightleftharpoons H \cdot CO \cdot OH$, and sodium formate is produced by passing carbon monoxide over soda-lime at 200° : $NaOH + CO = H \cdot CO \cdot ONa$. Carbon monoxide is, therefore, the anhydride of formic acid. The anhydride of oxalic acid, C_2O_3 , does not exist but breaks up at once into $CO + CO_2$.

Properties of carbon monoxide.—Carbon monoxide is a colourless gas with a peculiar faint smell. It is *very poisonous*, 10 ml. per kg. weight of an animal produces death, and the inhalation of air containing

1 vol. of CO in 800 vols. is fatal in half an hour. Coal gas (especially modern gas, which contains water-gas) owes its poisonous properties to carbon monoxide. Carbon monoxide is not poisonous to green plants or soil bacteria, which oxidise it.

The poisonous action of carbon monoxide depends on its absorption by the haemoglobin of the blood to form bright-red *carboxyhaemoglobin*, which is very stable and not decomposed by oxygen. Poisoning with carbon monoxide may be detected by the absorption spectrum of the blood. In cases of poisoning artificial respiration and administration of oxygen should be resorted to at once and prolonged for hours if necessary, the patient being kept warm and at rest; alcohol may be given if there is a tendency to fainting.

Carbon monoxide is liquefied with difficulty; its critical temperature is -138.7° and the critical pressure 34.6 atm. The liquid boils at -191.5° and solidifies at -200° . The gas is sparingly soluble in water but is readily absorbed by a solution of cuprous chloride in hydrochloric acid, a compound being formed which can be obtained in white crystals, $\text{CuCl}\cdot\text{CO}\cdot 2\text{H}_2\text{O}$. It is also absorbed by a solution of cuprous chloride in ammonia, but cuprous chloride in dry alcohol does not absorb the gas. It is absorbed by solid cuprous chloride *under pressure*, forming $\text{CuCl}\cdot\text{CO}$.

The composition of carbon monoxide is determined by passing it over heated copper oxide, the carbon dioxide formed being absorbed in weighed potash-bulbs. If the composition of carbon dioxide is assumed (see p. 621), that of carbon monoxide may be found. On exploding a moist mixture of 2 volumes of the gas with 1 volume of oxygen, 2 volumes of carbon dioxide (absorbable by potash) are formed: $2\text{C}_x\text{O}_y + \text{O}_2 = 2\text{CO}_2$. Hence $x=y=1$, and the formula is CO. This is confirmed by the density.

Many metals form compounds called *carbonyls* with carbon monoxide (see p. 950). Carbon monoxide penetrates heated iron and may escape through the iron flues of stoves burning with an insufficient supply of air. Carbon monoxide combines directly with chlorine, forming carbonyl chloride (*phosgene*), COCl_2 . It reduces iodine pentoxide at 90° , with liberation of iodine: $\text{I}_2\text{O}_5 + 5\text{CO} = \text{I}_2 + 5\text{CO}_2$, a reaction which is used for the estimation of carbon monoxide. If a gas containing only 0.05 per cent of CO is shaken with a solution of palladous chloride, a black precipitate of palladium is produced.

Combustion of carbon monoxide.—Carbon monoxide burns in air or oxygen with a bright blue flame, forming carbon dioxide. It is a powerful reducing agent, and when passed over heated metallic oxides it abstracts the oxygen: $\text{PbO} + \text{CO} = \text{Pb} + \text{CO}_2$. Carbon monoxide is the active agent in a number of metallurgical processes, *e.g.* in the blast furnace.

A mixture of two volumes of carbon monoxide and one volume of oxygen explodes when sparked. H. B. Dixon (1880) found that if the gas is carefully dried by phosphorus pentoxide, it cannot be exploded in a eudiometer, although combination occurs locally in the path of the electric sparks. If a trace of moisture, or of any gas which contains

hydrogen and so produces water on combustion in oxygen ($\text{CH}_4, \text{H}_2\text{S}$, etc.), is added, the mixture can be exploded by a spark. M. Traube (1885) found that a burning jet of carbon monoxide, which has been dried with phosphorus pentoxide, is extinguished in a jar of air containing concentrated sulphuric acid which has been standing stoppered for a few hours.

Girvan (1903) found that 1 molecule of water in 21,000 of the gas is still active. The maximum effect is produced by 4.5 per cent of water vapour. Bone and Weston (1926) found that a very dry mixture is exploded by a very powerful electric spark, but the combustion is incomplete.

Since carbon monoxide reduces steam at high temperatures: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, Dixon supposed that this reaction first occurs, and that the hydrogen then combines with the oxygen present to reproduce water: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, and so on. Another theory suggests a reaction involving atomic hydrogen: (a) $\text{H} + \text{O}_2 + \text{CO} = \text{OH} + \text{CO}_2$; (b) $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$.

In some cases the presence of *pure* water is not sufficient to catalyse a reaction, but a trace of impurity is needed.

H. B. Baker (1902) found that a mixture of very pure hydrogen and oxygen from the electrolysis of barium hydroxide solution, if sealed up in glass tubes over purified P_2O_5 , combined slowly after prolonged drying when the tube was heated with a flame, or if a spiral of silver wire was heated almost to the melting point in the gas, *but no explosion occurred*. The water produced by the combination was, according to a theory proposed by H. E. Armstrong (1885), too pure to form an electrically-conducting circuit, which he considered necessary for chemical change:



The water normally forms a "closed conducting circuit," owing to traces of impurity, and the oxygen acts as a depolariser.

Catalytic effects of moisture.—Many cases of the catalytic effect of moisture are known. Dry chlorine does not combine with many dry metals, except mercury. Dry carbon monoxide and oxygen do not explode on sparking. In the absence of moisture, to the extent produced by prolonged drying over phosphorus pentoxide, carbon combines only slowly with oxygen on heating; ammonium chloride and calomel volatilise on heating without dissociation; ammonia and hydrogen chloride do not combine on mixing; and sulphur and phosphorus may be distilled unchanged in oxygen. Nitrogen trioxide, after prolonged drying in the liquid state over P_2O_5 , volatilises as N_4O_6 ; in presence of a minute trace of moisture this instantly dissociates into NO and NO_2 . The boiling point of liquid N_4O_6 is also raised from -2° to $+43^\circ$ by drying for three years. Calomel dried for six months over P_2O_5 at 115° will not vaporise at 352° , when its usual vapour pressure is 347 mm. Nitric oxide and oxygen, hydrogen and chlorine, and ammonia and carbon dioxide, do not react when very pure and dry. Sodium, potassium, and phosphorus scarcely react with dry oxygen, although dry boron, tellurium, arsenic, and antimony react readily under the usual conditions.

Producer gas.—The gas obtained by passing air through a bed of incandescent coke consists mainly of nitrogen and carbon monoxide; it is made for heating purposes and called producer gas (or air-gas).

The producer consists of a closed fire-grate in which coke rests on bars; it is often sealed below by water, and the *primary air* is either drawn through the fuel with a fan, or forced through by pressure, the ash-pit then being air-tight. If the gas is burnt without cooling, the total amount of heat evolved is the same as if the carbon were burnt directly to carbon dioxide; usually 30 per cent of the heat is lost by the producer gas cooling before it arrives at the place where it is burnt. Gas-firing is preferred for many purposes on account of the ease with which it is regulated and its cleanliness. The air admitted for the combustion of the producer gas is called *secondary air*.

If coal is used instead of coke, the gas will be mixed with coal gas unless the draught through the producer is downwards, when the coal gas is decomposed by the incandescent fuel. Otherwise the tar must be separated from the gas ("suction-gas"); with down-draught it is absent.

Water gas.—If steam is passed over incandescent coke a mixture of carbon monoxide, carbon dioxide, and hydrogen, called *water gas*, is formed: (1) $C + H_2O \rightleftharpoons CO + H_2$; (2) $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$. The carbon monoxide increases as the temperature rises, as is seen from the following table, giving the results of Bunte:

Temp. °C.	Percentage of steam decom- posed	Composition of gas by volume					
		H ₂	CO	CO ₂	CO	H ₂ CO	CO CO + CO ₂
675°	8.8	65.2	4.9	29.8	0.16	13.3	0.141
758	25.3	65.2	7.8	27.0	0.29	8.4	0.224
840	41.0	61.9	15.1	22.9	0.65	4.1	0.397
955	70.2	53.3	39.3	6.8	5.80	1.35	0.853
1010	94.0	48.8	49.7	1.5	33.10	0.98	0.972
1060	98.0	50.7	48.0	1.3	36.8	1.05	0.975
1125	99.4	50.9	48.5	0.6	80.8	1.05	0.988

Average water gas has the following composition by volume: H₂, 49.17; CO, 43.75; CO₂, 2.71; methane, 0.31; N₂, 4.00. Its calorific value is about 350 B.Th.U. per cu. ft., but as it requires only 2.5 vols. of air for combustion, it gives a very hot flame.

The reactions in the water gas producer absorb heat, hence the hot coke is gradually cooled by the steam blast and the amount of carbon dioxide in the gas increases. When the *steam blast* has passed for a certain time it is shut off, and an *air blast* turned on until the fuel is again heated to bright redness. The gas formed in the air-blow is usually turned to waste. To keep the temperature as uniform as possible, the steam blast is passed alternately upwards and downwards through the producer. In recent types the fuel bed is thin, and carbon dioxide is largely formed during the air-blow, which is short, say two minutes to eight minutes of steam blow.

Semi-water gas is prepared by passing a mixture of steam and air *continuously* through incandescent coke, the heat evolved by the combustion of the carbon with the oxygen of the air being sufficient to

maintain the temperature for the water gas reaction to occur with the steam. **Mond gas** is formed with a large excess of steam which keeps the temperature low (650°), and allows of the recovery as ammonia of a larger proportion of the nitrogen of the coal-slack used than if the coal had been heated in retorts.

Carburetted water gas is a mixture of water gas with hydrocarbons, partly unsaturated, which burn with a luminous flame. Water gas alone (*i.e.* a mixture of hydrogen, carbon monoxide, and nitrogen) burns with a blue non-luminous flame but may be used with Welsbach mantles for illuminating purposes, since it gives out much heat on combustion.

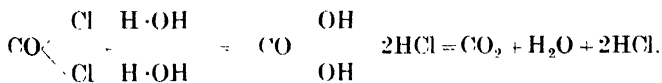
Pintsch gas is formed by spraying oil into hot retorts and passing the gas through a condenser, scrubber, and lime purifier.

The compositions of typical specimens of semi-water gas (producer gas), are given below, together with an analysis of true water gas :

	CO.	H ₂ .	CH ₄ .	CO ₂ .	O ₂ .	N ₂ .
Dowson gas from coal	25.07	18.73	0.62	6.57	—	49.01
„ from coke	22.40	7.00	—	4.90	0.50	65.20
Mond gas from coal	13.20	24.80	2.30	12.90	—	46.80
Water gas - - -	39.6	51.9	0.8	4.2	—	2.9

The calorific value of producer and semi-water gas is low, being usually about 125 B.Th.U. per cu. ft., as compared with about 600 for good coal gas and 350 for water gas.

Carbonyl chloride.—When a mixture of equal volumes of carbon monoxide and chlorine is exposed to bright sunlight, or passed over active charcoal, combination occurs to form carbonyl chloride or *phosgene*, COCl₂ (Greek, *phos*, light, and *gennao*, I produce). This compound, discovered by John Davy in 1811, is a colourless gas with a penetrating and suffocating odour, and very poisonous. It is readily liquefied by cooling, forming a colourless mobile liquid, b. pt. 8.2°. The gas does not fume in moist air, but is readily hydrolysed by water.



Phosgene is the chloride of carbonic acid. When the gas is passed into a solution of ammonia in toluene, urea is formed: $\text{COCl}_2 + 4\text{NH}_3 = \text{CO}(\text{NH}_2)_2 + 2\text{NH}_4\text{Cl}$. This is the diamide of carbonic acid. Both urea and ammonium chloride are precipitated, but may be separated by warming with alcohol, in which urea is soluble. The alcoholic solution deposits crystals of urea on evaporation and cooling.

The monoamide of carbonic acid, HO·CO·NH₂, is called **carbamic acid**. Its ammonium salt NH₄O·CO·NH₂ is contained, with ammonium bicarbonate NH₄HCO₃, in commercial “carbonate of ammonia.”

Carbonyl bromide (COBr₂), is slowly formed from carbon monoxide and bromine vapour, but is best prepared by dropping concentrated sulphuric acid into carbon tetrabromide at 160°: $\text{CBr}_4 + \text{H}_2\text{SO}_4 = \text{COBr}_2 + \text{SO}_3 + 2\text{HBr}$. **Carbonyl fluoride** (COF₂ (m. pt. - 114°, b. pt. - 83°)) is formed by burning fluorine in carbon monoxide.



Carbonyl sulphide.—Carbonyl sulphide or *carbon oxysulphide* COS, discovered by Than in 1867, is formed when carbon monoxide and sulphur vapour are passed through a heated tube: $\text{CO} + \text{S} \rightleftharpoons \text{COS}$, or when sulphur dioxide is passed over red-hot charcoal: $3\text{C} + 2\text{SO}_2 = 2\text{COS} + \text{CO}_2$. It is prepared by the action of diluted sulphuric acid (5 vols. of H_2SO_4 to 4 vols. of water) on ammonium thiocyanate NH_4CNS at 20° . The unstable thiocyanic acid first formed is hydrolysed: $\text{HCNS} + \text{H}_2\text{O} = \text{COS} + \text{NH}_3$.

The gas contains hydrocyanic acid HCN and carbon disulphide. The first is removed by passing through very concentrated potassium hydroxide solution, the latter by passing through concentrated sulphuric acid followed by a mixture of trimethyl phosphine $\text{P}(\text{CH}_3)_3$, pyridine, and nitrobenzene. Pure carbonyl sulphide is formed by decomposing potassium ethyl thiocarbonate (*Bender's salt*) with dilute hydrochloric acid: $\text{C}_2\text{H}_5\text{O}\cdot\text{CS}\cdot\text{OK} + \text{HCl} = \text{COS} + \text{KCl} + \text{C}_2\text{H}_5\text{OH}$.

Carbonyl sulphide is a colourless odourless gas, moderately soluble in water, readily soluble in toluene. It liquefies at 0° under 12.5 atm. pressure, b. pt. -50.2° , m. pt. -138.2° . It is very inflammable, a glowing chip causing ignition, and burns with a blue slightly luminous flame. When mixed with oxygen it explodes feebly with a spark, but not always after drying with phosphorus pentoxide: $2\text{COS} + 3\text{O}_2 = 2\text{CO}_2 + 2\text{SO}_2$. A heated platinum spiral decomposes the gas without change of volume into sulphur and carbon monoxide: $\text{COS} = \text{CO} + \text{S}$ (solid); the reaction $2\text{COS} = \text{CS}_2 + \text{CO}_2$ also occurs. The molecule $\text{O}=\text{C}=\text{S}$ is linear.

The solution of carbonyl sulphide is slowly hydrolysed: $\text{COS} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{S}$. The mineral waters of Harkány and Parád in Hungary appear to contain carbonyl sulphide. Carbonyl sulphide is absorbed by dilute aqueous or alcoholic potash with the formation of a mixture of sulphide and carbonate: $\text{COS} + 4\text{KOH} = \text{K}_2\text{CO}_3 + \text{K}_2\text{S} + 2\text{H}_2\text{O}$.

Formic acid.—At 120° under 3 to 4 atm. pressure carbon monoxide is rapidly and completely absorbed by a concentrated solution of sodium hydroxide, sodium formate being produced: $\text{NaOH} + \text{CO} = \text{H}\cdot\text{COONa}$. From this, anhydrous formic acid $\text{H}\cdot\text{COOH}$ is obtained cheaply and in quantity. Thirty-five parts of concentrated sulphuric acid are run into 200 parts of concentrated formic acid, with shaking. To this mixture 50 parts of sodium formate and 50 parts of concentrated sulphuric acid are added alternately and the liquid is distilled.

Formic acid is a colourless liquid with a pungent odour, density 1.226, b. pt. 100.6° , m. pt. 8.43° . It acts violently on the skin, raising blisters. The acid is contained in red ants (*Formica rufa*), and was first obtained from them by distillation by Samuel Fisher, whose results were published by John Ray in 1671. It is also present in nettles and in nearly all stinging organisms.

Formates are powerful reducing agents. Mercuric oxide dissolves in dilute formic acid as mercuric formate. This is soon reduced to a white precipitate of mercurous formate, and finally to grey metallic mercury. The formic acid is oxidised to carbon dioxide. In presence

of ruthenium, rhodium, and iridium, especially if traces of sulphides are present, formic acid decomposes into carbon dioxide and hydrogen : $\text{H}_2\text{CO}_2 = \text{CO}_2 + \text{H}_2$. The reverse reaction occurs on electrolytic reduction with a clean zinc cathode, or by passing hydrogen through a solution of a bicarbonate containing colloidal palladium or platinum.

If a mixture of sodium formate with one-twentieth of its weight of sodium hydroxide is heated at $250^\circ\text{--}260^\circ$, hydrogen is evolved and sodium oxalate remains : $2\text{HCO}_2\text{Na} (\text{CO}_2\text{Na})_2 + \text{H}_2$. From sodium oxalate free oxalic acid $(\text{CO}_2\text{H})_2, 2\text{H}_2\text{O}$ is obtained. By electrolytic reduction of oxalic acid, glyoxylic acid $\text{H}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, and finally glycollic acid $\text{H}_2(\text{OH})\text{C}\cdot\text{CO}_2\text{H}$ are obtained. All these compounds may be obtained from carbon monoxide.

Carbon suboxide.—If malonic acid $\text{CH}_2(\text{COOH})_2$ or ethyl malonate $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$ is heated with a large excess of phosphorus pentoxide at 300° under 12 mm. pressure, carbon suboxide C_3O_2 is evolved. The reaction with malonic acid is : $\text{CH}_2(\text{COOH})_2 - \text{C}_3\text{O}_2 + 2\text{H}_2\text{O}$, that with ethyl malonate is : $\text{CH}_2(\text{COOC}_2\text{H}_5)_2 - \text{C}_3\text{O}_2 + 2\text{H}_2\text{O} + 2\text{C}_2\text{H}_4$.

The gas evolved is liquefied by cooling and fractionated ; the carbon suboxide boils at 6° . It freezes in liquid air to a white solid, m. pt. -111.3° . The gas has a pungent odour and is poisonous. It burns in air with a smoky flame, and explodes with oxygen when sparked : $\text{C}_3\text{O}_2 + 2\text{O}_2 = 3\text{CO}_2$. The liquid slowly polymerises at the ordinary temperature, forming a red solid insoluble in water, and the gas decomposes rapidly on heating or in contact with phosphorus pentoxide. Carbon suboxide dissolves in water, forming a solution of malonic acid, of which it is the second anhydride, *i.e.* formed by the removal of *two* molecules of water from one molecule of the acid. Its formula is $\text{O}:\text{C}:\text{C}:\text{C}:\text{O}$ and the molecule is linear. The gas is readily soluble in benzene and xylene.

Carbon disulphide.—Sulphur vapour when passed over red-hot carbon produces carbon disulphide CS_2 , a volatile liquid. The reaction from solid sulphur and carbon is endothermic : $\text{C} + 2\text{S} = \text{CS}_2 - 19.0$ k. cal., but the reaction with sulphur vapour is exothermic. Carbon disulphide was discovered by Lavoisier (1796) by heating pyrites with charcoal.

A vertical cast-iron or fireclay retort (Fig. 325) set in a furnace, is filled with charcoal. Sulphur is fed in through a tube, being kept fused by the waste heat. The sulphur volatilises, and the vapour passes over the charcoal at $800^\circ\text{--}900^\circ$, forming carbon disulphide. The vapour passes through a small iron cylinder, where sulphur is deposited, and the carbon disulphide is condensed in a very long worm-tube cooled by water.

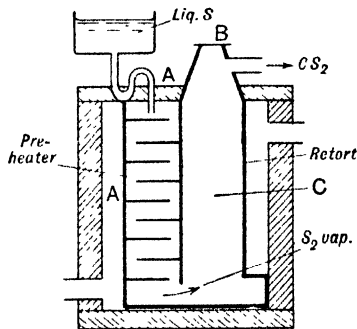


FIG. 325.—Carbon disulphide retort.

In Taylor's electrical process (1899), used in America, a tower is packed with charcoal or coke. Below is a furnace with four carbon electrodes,

between alternate pairs of which an arc is struck. The sulphur in the lower part of the furnace melts and evaporates, the vapour passing through the heated coke above the arc, and forming carbon disulphide.

Carbon disulphide is purified by distillation over lead acetate, or by agitation with mercury until it no longer blackens it, after which it is redistilled over white wax and then over phosphorus pentoxide.

On the small scale, carbon disulphide can be prepared as follows. A combustion tube is packed with recently ignited charcoal, and the lower end is connected with bulb tubes surrounded by ice (Fig. 326). The tube is

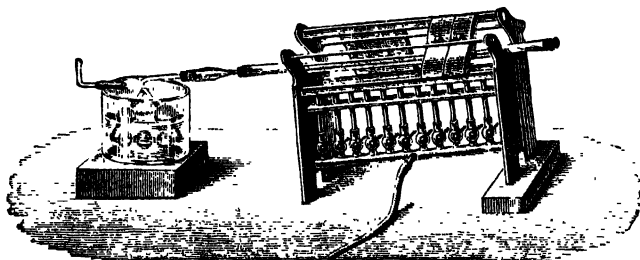


Fig. 326.—Preparation of carbon disulphide.

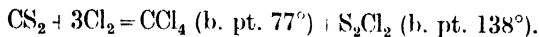
heated to redness and bits of sulphur are introduced into the upper end, which is corked. The sulphur vapour passes over the hot charcoal, and carbon disulphide collects in the bulbs.

Carbon disulphide is a colourless mobile strongly refracting liquid, which boils at 46.25° , solidifies at -116° , and remelts at -112.8° . Its density at 0° is 1.2923. It is almost insoluble in water: 100 ml. of water dissolve 0.204 gm. of CS_2 at 0° , 0.179 at 20° , and 0.014 at 49° . Carbon disulphide mixes with absolute alcohol, ether, and oils. It dissolves sulphur, white phosphorus, indiarubber, camphor, resins, etc., and is used as a solvent, but it is mostly used to make viscose (artificial silk) by the xanthate process. Carbon disulphide readily volatilises. Its vapour has usually an exceedingly unpleasant smell which is removed by careful purification, when the liquid smells of chloroform, but the smell soon becomes unpleasant again. It is poisonous and is used to kill moths in furs and rats and mice in grain elevators. The vapour has a relatively low ignition temperature: a test-tube filled with hot oil held over the liquid in a dish sets fire to the vapour. The vapour mixed with air or oxygen explodes when kindled, the most violent explosion being obtained with $2\text{CS}_2 + 5\text{O}_2 = 2\text{CO} + 4\text{SO}_2$. Sulphur dioxide, sulphur trioxide, carbon monoxide, and carbon dioxide are formed, and no free carbon is deposited.

If a little mercury fulminate is exploded in a tube filled with carbon disulphide vapour, decomposition commences with separation of sulphur and carbon, but is not propagated through the vapour.

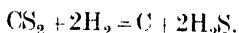
Carbon disulphide vapour is decomposed by heated potassium: $\text{CS}_2 + 4\text{K} = 2\text{K}_2\text{S} + \text{C}$. When chlorine is passed into boiling carbon

disulphide containing a little iodine, carbon tetrachloride CCl_4 is formed :



Both products are useful and are separated by fractional distillation. Carbon tetrachloride is used as a grease solvent, and under the name of *Pyrene* for extinguishing fires (*not sodium !*).

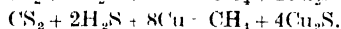
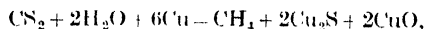
A mixture of carbon disulphide vapour and hydrogen when passed over heated nickel at 450° yields hydrogen sulphide :



This reaction is used in determining the amount of CS_2 in coal gas : the H_2S is estimated by passing the gas through a solution of lead nitrate in sugar syrup, and matching the brown tint of the PbS with standards.

Carbon disulphide reacts with a solution of triethyl phosphine $\text{P}(\text{C}_2\text{H}_5)_3$ in ether, forming a red crystalline compound $\text{P}(\text{C}_2\text{H}_5)_3 \cdot \text{CS}_2$.

When carbon disulphide vapour is passed over red-hot copper, carbon is deposited and copper sulphide formed : $\text{CS}_2 + 4\text{Cu} = \text{C} + 2\text{Cu}_2\text{S}$. In this way the composition was first determined by Vauquelin. A mixture of the vapour with steam or hydrogen sulphide when passed over red-hot copper gives methane :



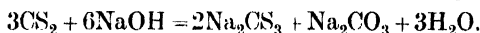
From methane, organic substances such as alcohol and acetic acid may be obtained, so that these reactions allow of their synthesis (Berthelot, 1856-8).

Carbon subsulphide. C_3S_2 , corresponding with the suboxide C_3O_2 , was discovered by Lengyel (1893). It is formed by striking an arc under carbon disulphide, the cathode being of carbon, and the anode zinc, or antimony containing 7 per cent of carbon : $3\text{CS}_2 = 4\text{Zn} + \text{C}_3\text{S}_2 + 4\text{ZnS}$. The liquid is distilled *in vacuo* and the vapour condensed at -40° . A yellowish-red solid is formed, m. pt. -0.5° . It has the composition C_3S_2 , and the structural formula is probably $\text{S}:\text{C}:\text{C}:\text{C}:\text{S}$, similar to that of C_3O_2 . The vapour has an offensive odour, and produces a copious flow of tears. A bromide $\text{C}_3\text{S}_2\text{Br}_6$, formed directly, has a not unpleasant aromatic smell. **Carbon monosulphide** CS is said to be contained in a polymerised form in the brown powder formed when carbon disulphide is exposed to light, and gaseous carbon monosulphide and ozone are formed in the slow combustion of carbon disulphide vapour.

Thiocarbonyl chloride CSCl_2 is formed when a mixture of phosphorus pentachloride and carbon disulphide is heated in a sealed tube at 100° : $\text{PCl}_5 + \text{CS}_2 = \text{PSCl}_3 + \text{CSCl}_2$. It is best prepared by first making **thiocarbonyl perchloride** CSCl_4 by passing dry chlorine into carbon disulphide containing a little iodine at $20-25^\circ$: $2\text{CS}_2 + 5\text{Cl}_2 = 2\text{CSCl}_4 + \text{S}_2\text{Cl}_2$, hydrolysing the sulphur chloride with hot water, and reducing the thiocarbonyl perchloride with tin and hydrochloric acid. It is a liquid, boiling at 73.5° with slight decomposition, has a very offensive odour, and is slowly hydrolysed by water.

Carbon sulphoselenide CSSe , and sulphotelluride CSTe , are formed by striking an arc under carbon disulphide between a graphite cathode and an anode of graphite and selenium, or tellurium, respectively. They are yellow and red liquids, respectively.

Thiocarbonic acid.—Carbon disulphide when shaken with a concentrated sodium hydroxide solution slowly dissolves, forming sodium carbonate and sodium thiocarbonate Na_2CS_3 , which may be regarded as the carbonate in which oxygen is replaced by sulphur (Berzelius, 1826):



With a solution of sodium sulphide reaction is more rapid, and sodium thiocarbonate alone is formed: $\text{Na}_2\text{S} + \text{CS}_2 = \text{Na}_2\text{CS}_3$. The pure salt is obtained by adding CS_2 to an alcoholic solution of NaHS . On adding ether, pinkish-yellow crystals, $\text{Na}_2\text{CS}_3 \cdot \text{H}_2\text{O}$, of the thiocarbonate separate. A deep red solution and yellow crystals of ammonium thiocarbonate $(\text{NH}_4)_2\text{CS}_3$, are formed when carbon disulphide and concentrated ammonia are allowed to stand together for a few days.

Free thiocarbonic acid H_2CS_3 is obtained as a bright red liquid by dropping crystals of $(\text{NH}_4)_2\text{CS}_3$ into a large excess of concentrated hydrochloric acid. Ammonium perthiocarbonate $(\text{NH}_4)_2\text{CS}_4$ is obtained together with the thiocarbonate by refluxing $(\text{NH}_4)_2\text{S}_5$ solution with carbon disulphide; prolonged action gives orange-yellow crystals of $(\text{NH}_4)_2\text{CS}_3$, but incomplete action gives yellow crystals of $(\text{NH}_4)_2\text{CS}_4$, which are washed with carbon disulphide and ether. On adding this salt to 98 per cent formic acid, perthiocarbonic acid H_2CS_4 , not quite pure, is formed. With hydrochloric acid only H_2CS_3 and sulphur are formed. (Mills and Robinson, 1928).

Thiocarbonates are used in destroying *Phylloxera*, a kind of aphid infesting vines. Carbon disulphide is a poison for this insect but is too volatile to use directly; if the plants are sprayed with a solution of sodium thiocarbonate, this is slowly decomposed by atmospheric carbonic acid, with liberation of carbon disulphide.

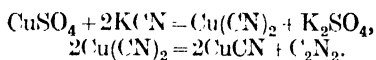
Thiocarbonates give a brown precipitate of CuCS_3 with copper salts; a red precipitate of PbCS_3 with lead salts; and a yellow precipitate of Ag_2CS_3 with dilute silver nitrate. These rapidly become black from formation of sulphides. Ferric salts give a red colour.

If carbon disulphide is dissolved in alcoholic potash, potassium xanthate $\text{KS} \cdot \text{CS} \cdot \text{OC}_2\text{H}_5$ is formed. It is decomposed by acids with liberation of carbon disulphide and alcohol; this indicates that the ethyl radical is attached to oxygen and not to sulphur.

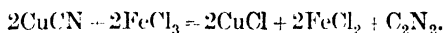
Cyanogen, discovered by Gay-Lussac (1815), is evolved on heating the cyanides of silver, mercury, and gold, the most convenient being mercuric cyanide $\text{Hg}(\text{CN})_2$, which is heated to dull redness in a hard glass or steel tube: $\text{Hg}(\text{CN})_2 = \text{Hg} + \text{C}_2\text{N}_2$. A heavy brown non-volatile powder produced at the same time, called **paracyanogen**, is probably a polymerised form of cyanogen $(\text{CN})_n$; it decomposes slowly into cyanogen at 800° . Cyanogen gas is evolved at a lower temperature if mercuric chloride is mixed with the cyanide: $\text{Hg}(\text{CN})_2 + \text{HgCl}_2 = \text{Hg}_2\text{Cl}_2 + \text{C}_2\text{N}_2$

Heat a little mercuric cyanide in a hard glass tube fitted with a rubber stopper and brass jet. Ignite the gas at the jet; it burns with a characteristic peach-blossom coloured flame. *N.B.*—Cyanogen is very poisonous.

An economical method of preparation of cyanogen (which is not pure, but contains some carbon dioxide and hydrocyanic acid) is to drop concentrated potassium cyanide solution into a warm solution of 2 parts of crystallised copper sulphate in 4 parts of water. Cupric cyanide $\text{Cu}(\text{CN})_2$, first formed as a yellow precipitate, quickly decomposes into cyanogen gas and white cuprous cyanide:



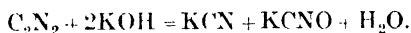
If the cuprous cyanide is warmed with ferric chloride solution, the rest of the cyanogen is evolved:



Cyanides are formed by the action of nitrogen on carbides at high temperatures: if nitrogen is passed over barium carbide, or an intimate mixture of barium oxide and carbon, at a red heat, barium cyanide is produced: $\text{BaO} + 3\text{C} + \text{N}_2 = \text{Ba}(\text{CN})_2 + \text{CO}$. Small amounts of cyanogen are present in blast-furnace gas.

Cyanogen is a colourless gas, soluble in 4 vols. of water, and must be collected over mercury. It has a smell of bitter almonds and is very poisonous. When cooled it condenses to a colourless liquid, boiling at -20.7° , which freezes below -35° to a white solid, melting at -27.92° . The density of the gas shows that it has the formula C_2N_2 . It is an endothermic compound: 2C (graphite) + $\text{N}_2 = \text{C}_2\text{N}_2 - 70$ k. cal.

Cyanogen is absorbed by potassium hydroxide solution to form potassium cyanide KCN and potassium cyanate KCNO:



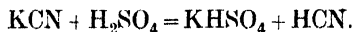
With water at 0° the reaction $\text{C}_2\text{N}_2 + \text{H}_2\text{O} = \text{HCN} + \text{HCNO}$ occurs. These reactions are like those with chlorine. All compounds of cyanogen contain the univalent cyanogen group or radical CN, and the latter is sometimes written Cy, since it behaves to some degree as an element. In solutions of cyanides the cyanide ion CN' is formed: $\text{KCN} = \text{K}' + \text{CN}'$.

A solution of cyanogen in water decomposes on standing, depositing a brown precipitate: the solution then contains ammonium oxalate, hydrocyanic acid (HCN), urea, carbon dioxide, etc.

A mixture of equal volumes of cyanogen and oxygen explodes on ignition or with an electric spark, even when carefully dried with phosphorus pentoxide, forming carbon monoxide and nitrogen: $\text{C}_2\text{N}_2 + \text{O}_2 = 2\text{CO} + \text{N}_2$; with double the volume of oxygen, the monoxide is burnt to carbon dioxide. In the last case, 1 vol. of cyanogen gives 2 vols. of carbon dioxide (absorbed by alkali) and 1 vol. of nitrogen. This shows that 1 molecule of cyanogen contains two atoms of carbon and 1 molecule or 2 atoms of nitrogen, and the formula is C_2N_2 .

The formula of cyanogen may be written as $\text{N} : \text{C} : \text{C} : \text{N}$, which agrees with its reduction to ethylenediamine, $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$.

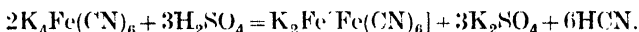
Hydrocyanic acid.—When potassium cyanide is distilled with a mixture of equal volumes of sulphuric acid and water, the vapour of hydrocyanic acid HCN is evolved :



(With *concentrated* sulphuric acid, carbon monoxide is formed in large quantities : $\text{HCN} + 2\text{H}_2\text{O} = \text{H}\cdot\text{COOH} + \text{NH}_3 = \text{H}_2\text{O} + \text{CO} + \text{NH}_3$.) The gas is dried by a U-tube of calcium chloride and passed into a second U-tube cooled in ice. A colourless liquid, boiling at 25° and freezing at -15° , collects. This is anhydrous hydrocyanic acid. The anhydrous acid is best made by passing pure hydrogen sulphide slowly over dry mercuric cyanide heated to 30° in a long glass tube, and condensing the liquid in a freezing mixture : $\text{Hg}(\text{CN})_2 + \text{H}_2\text{S} = \text{HgS} + 2\text{HCN}$. Hydrocyanic acid is formed when acetylene is sparked with nitrogen : $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{HCN}$; when a mixture of nitrogen, methane, and hydrogen is passed through a carbon arc : $2\text{CH}_4 + \text{N}_2 = 2\text{HCN} + 3\text{H}_2$. and, according to Scheele, when ammonia gas is passed over strongly heated charcoal.

Hydrocyanic acid vapour burns with a purple flame in air, and a mixture with oxygen explodes when sparked : $4\text{HCN} + 5\text{O}_2 = 2\text{N}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O}$. Its composition may be found in this way.

Anhydrous hydrocyanic acid is a really dangerous poison ; its preparation should be undertaken only by an expert chemist. A dilute solution may be prepared by distilling potassium ferrocyanide with dilute sulphuric acid (1 acid + 2 water) :



The 2½ per cent solution is used as a constituent of remedies for bronchial catarrh, etc., and is called *prussic acid*. In this concentration it is also very poisonous.

The smell of bruised fruit kernels, laurel leaves and moist bitter almonds is due to hydrocyanic acid, and it is a curious fact that Scheele, the discoverer of hydrocyanic acid (1782), did not know of its poisonous properties : these were first suspected from its formation from the poisonous bitter almonds by distillation with water. Ammonia, or chlorine water, is used as an antidote, although larger doses are almost instantaneously fatal. The best antidote is said to be ferrous hydroxide, obtained by adding 1.5 gm. of sodium hydroxide in 300 ml. of water and 2 gm. of magnesia to 7.5 gm. of ferrous sulphate crystals in 300 ml. of water.

Hydrocyanic acid is a very weak monobasic acid : its salts with alkali metals, the cyanides, are hydrolysed in solution, which has an alkaline reaction and a smell of peach-kernels owing to the presence of the free acid : $\text{CN}' + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}'$.

Although organic derivatives with structures $\text{R}^{\ominus}\text{C}::\text{N}^{\oplus}$ or $\text{R}-\text{C}\equiv\text{N}$ (cyanides), and $\text{R}^{\ominus}\text{N}::\text{C}:$ or $\text{R}-\text{N}\rightarrow\text{C}$ (isocyanides) are isomeric, the cyanide ion from the two corresponding acids is identical, $[:\text{N}::\text{C}:]$.

Cyanogen Chloride.—If chlorine is passed into aqueous hydrocyanic acid cyanogen chloride $\text{CN}\cdot\text{Cl}$ is formed, and may be condensed in a freezing

mixture to a colourless mobile liquid, b. pt. 12.7° (Berthollet, 1787). The liquid if slightly acidified, rapidly polymerises to white solid **cyanuric chloride** $(\text{CNCl})_3$. Cyanogen chloride reacts with alkalis forming a chloride and a cyanate: $\text{CN}\cdot\text{Cl} + 2\text{KOH} = \text{KCl} + \text{KCNO} + \text{H}_2\text{O}$. With ammonia it forms **cyanamide** $\text{CN}\cdot\text{NH}_2$.

Cyanogen chloride is best prepared by acting on sodium cyanide, a little water, and carbon tetrachloride, with chlorine gas and distilling. It is used in place of hydrocyanic acid for fumigation, since it is a lachrymatory gas and is easily detected.

Bromine reacts with hydrocyanic acid or potassium cyanide to form white crystalline **cyanogen bromide** $\text{CN}\cdot\text{Br}$; iodine reacts with potassium cyanide to form white needles of **cyanogen iodide** $\text{CN}\cdot\text{I}$. The latter may occur as an impurity in crude iodine. All the halogen compounds of cyanogen are very poisonous.

Tests for cyanides.—(1) A solution of a cyanide gives with silver nitrate a white curdy precipitate of **silver cyanide** AgCN , soluble in boiling concentrated nitric acid. (2) To the solution of the cyanide sodium hydroxide is added, and a few drops of a mixed solution of ferrous sulphate and ferric chloride: on warming a **ferrocyanide** is produced: (a) $\text{FeSO}_4 + 2\text{KCN} = \text{K}_2\text{SO}_4 + \text{Fe}(\text{CN})_2$; (b) $4\text{KCN} + \text{Fe}(\text{CN})_2 = \text{K}_4\text{Fe}(\text{CN})_6$. The dirty-brown precipitate is warmed with concentrated hydrochloric acid, which dissolves the ferric hydroxide present and leaves dark blue **Prussian blue**, formed by the action of the ferrocyanide on the ferric salt. If only traces of cyanides are present, a blue or green coloration appears. This test will detect 1 part of HCN in 50,000 parts of water. (3) The solution is evaporated to dryness on a water-bath with yellow ammonium sulphide, when a **thiocyanate**, e.g. KCNs , is formed: $(\text{NH}_4)_2\text{S}_2 + \text{KCN} = \text{KCNs} + (\text{NH}_4)_2\text{S}$ (volatile). The residue is dissolved in water and ferric chloride solution added: a blood-red coloration of ferric thiocyanate $\text{Fe}(\text{CNS})_3$ is formed.

Cyanates.—Fused potassium and sodium cyanides are powerful *reducing agents*: metallic oxides are converted into the metals and a cyanate is formed: $\text{KCN} + \text{PbO} = \text{KCNO} + \text{Pb}$. The cyanate may be extracted with water. When the solution is acidified, **cyanic acid** HCNO is formed but is almost completely decomposed with formation of ammonia and evolution of carbon dioxide: $\text{HCNO} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2$. Pure cyanic acid is a colourless liquid obtained by heating crystalline **cyanuric acid** $(\text{CNOH})_3$, obtained by distilling urea.

Ammonium cyanate NH_4CNO , obtained in solution by mixing concentrated solutions of potassium cyanate and ammonium chloride, is readily converted on heating into the isomeric urea: $\text{NH}_4\text{CNO} = \text{CO}(\text{NH}_2)_2$. This reaction was discovered by Wöhler in 1828. Previously urea had been obtained by John Davy in 1811, from phosgene and ammonia, but he was not aware of the nature of the products of the reaction.

FLAME

A flame is a zone in which chemical reaction between gases is occurring, accompanied by the evolution of heat and light: briefly, it is composed of glowing gas (Van Helmont, 1648). Transparent gases such

as nitrogen or oxygen do not glow when heated in tubes to a high temperature, nor do burning solids emit flame unless a vapour is formed. Iron burns in oxygen without flame; carbon burns in air at low temperatures without flame, but at high temperatures, when carbon monoxide is formed, this gas burns with a flame. A flame of pure hydrogen burning in dust-free air does not emit a visible light.

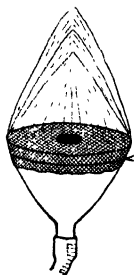


FIG. 327.—Experiment to demonstrate that a flame is hollow.

Thirty ml. of 30 per cent hydrogen peroxide are added in a dark room to a mixture of 10 ml. of 10 per cent pyrogallol solution, 20 ml. of saturated potassium carbonate solution, and 10 ml. of commercial formaldehyde. An orange-red glow, accompanied by a vigorous reaction, is seen. Light of the wave-length emitted is found to accelerate the reaction, which involves the oxidation of the pyrogallol.

Unless the combustible gas and the supporter of combustion are mixed before kindling the flame, the latter is *hollow* and occupies only the surface of contact of the two gases.

Depress a piece of new asbestos paper on a Bunsen flame: a dark ring is formed by the section of the flame. This may be seen also if a piece of ordinary paper is *quickly* lowered on to the flame.

Thrust a match-head quickly inside a Bunsen flame; or support the match, head upwards, in the metal tube by a pin stuck through it, and then kindle the flame. The match-head does not ignite for some time.

Stretch a piece of fine wire gauze over a funnel, and place a *small* heap of gunpowder in the centre of it (Fig. 327). Pass a rapid stream of coal gas through the funnel, and ignite the gas from above. The powder remains in the centre of the flame without explosion. If the flame is slowly turned down, the gunpowder ignites.

Insert one end of a glass tube into the middle of a Bunsen flame. Unburnt gas passes up the tube, and may be kindled at the upper end.

The terms *combustible* and *supporter of combustion* are relative, and depend on which gas is inside and which outside the flame.

A lamp chimney with a brass or tinplate top (Fig. 328) is fitted with a cork and tubes as shown. Coal gas is passed in and kindled at the top. At the same time air is drawn in through the second tube, and if a lighted taper is passed through this tube

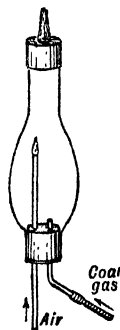


FIG. 328.—Air burning in coal gas.

into the chimney, the air ignites and burns in the coal gas with a blue non-luminous flame. A taper passed down to the air-flame cannot be kindled, since it is surrounded by an atmosphere of coal gas, but a jet of air may be ignited.

If the supply of coal gas is reduced, the upper flame shrinks and becomes less luminous, whilst the lower flame increases in size, since the oxygen has now less coal gas available, and the combustion extends over a larger space.

Arrange a glass cylinder with two tubes as shown in Fig. 329. Pass coal gas through *A*, and kindle a large flame at the top. Push *B* to the upper part of this flame and pass in a slow stream of oxygen. Lower *B*, when a flame of oxygen will be seen burning inside the first flame, the oxygen reacting with the unburnt gas in the centre of the hollow flame. By lowering *B* further the oxygen flame burns in the coal gas in the cylinder.

An accurate account of the structure of flame was given by Hooke (*Lampas*, 1677). He speaks of "that transient shining body which we call flame" as "nothing but the parts of the oyl rarified and raised by heat into the form of a vapour or smook, the free air that encompasseth this vapour keepeth it into a cylindrical form, and by its dissolving property preyeth upon those parts of it that are outwards . . . producing the light which we observe; but those parts which rise from the wick which are in the middle are not turned to shining flame till they rise towards the top of the cone, where the free air can reach and so dissolve them. With the help of a piece of glass [pressed upon the flame] anyone will plainly perceive that all the middle of the cone of flame neither shines nor burns, but only the outer superficies thereof that is contiguous to the free and unsaturated air."

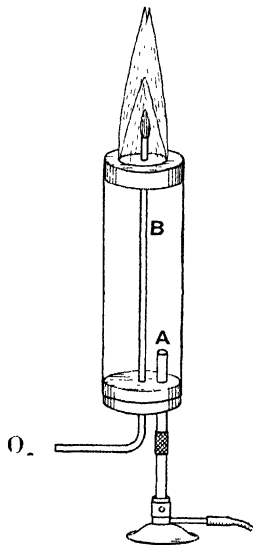


FIG. 329.—Oxygen burning inside a coal gas flame.

This description refers to a candle or oil-lamp flame. The candle and lamp consist of a cotton wick, surrounded by combustible material. The liquid oil or melted wax rises in the wick by capillary attraction. The top of the wick becomes incandescent, and the fuel decomposes, the combustible gas formed burning with a flame.

Attempt to kindle a piece of lump sugar by a taper: the sugar melts but will not take fire. Now rub a corner of the sugar with a small quantity of cigarette ash: the sugar can then readily be lighted at that point and burns with a flame.

The wick of the modern candle is plaited so that it bends over and is continuously consumed in the outer part of the flame. The wick presents the combustible material to the heated zone owing to its capillary structure, and it prevents too rapid conduction of heat from the heated point.

The structure of flame.—A hydrogen or carbon monoxide flame burning in air or oxygen consists (Fig. 330) of two cones, an inner *A* of unburnt

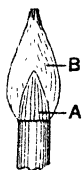


FIG. 330.—Hydrogen or carbon monoxide flame (two cones).

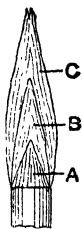
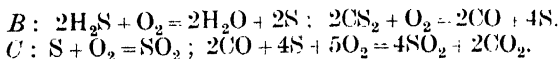


FIG. 331.—Carbon disulphide, cyanogen, or ammonia flame (three cones).

gas and an outer *B*, in which the single chemical reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ or $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ occurs. The flame of ammonia in oxygen consists of three cones, an inner *A* (Fig. 331) of unburnt gas, surmounted by a yellow cone *B*, in which decomposition of ammonia is taking place: $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$, and an outer pale greenish-yellow cone *C*,

in which the hydrogen burns. The nitrogen largely escapes combustion. A flame of hydrogen sulphide, cyanogen, or carbon disulphide vapour in oxygen or air is similar: with cyanogen the cone *B* is pink and corresponds with the reaction: $\text{C}_2\text{N}_2 + \text{O}_2 = 2\text{CO} + \text{N}_2$, whilst the cone *C* is greenish and represents complete combustion of the carbon monoxide.



Hydrocarbon flames contain four regions first defined by Berzelius (1822). The flame of a candle or of coal gas (Fig. 332) consists of (*a*)

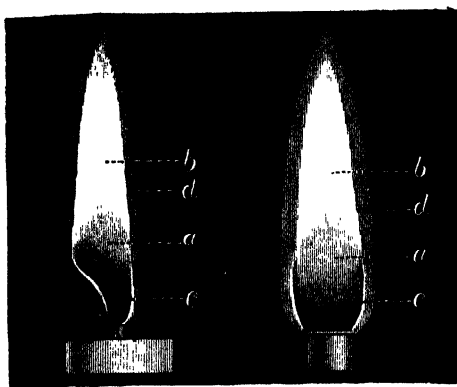


FIG. 332.—Structure of hydrocarbon flames.

the dark inner cone of unburnt gas or vapour; (*b*) a yellowish-white brightly luminous region, occupying most of the flame; (*c*) a small bright blue region at the base of the flame; (*d*) a faintly-visible outer mantle, completely sur-

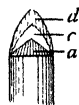


FIG. 333.—Small hydrocarbon flame with continuous blue region *c*.

rounding the flame. If the supply of gas is reduced, the flame shrinks, the luminous area *b* gradually disappearing, whilst the region *c* becomes continuous and constitutes an inner cone (Fig. 333). The regions *a* and *d* remain.

The luminosity of flame.—Why are the candle, coal gas and ethylene flames luminous, those of hydrogen and carbon monoxide non-luminous?

There are two principal theories to account for the luminosity of flame :

(1) **Davy's theory** (1816) : luminosity is due to particles of *solid carbon*, produced by thermal decomposition of the combustible, and heated to incandescence in the flame.

(2) **Frankland's theory** (1861) : luminosity is due to incandescent *vapours of dense hydrocarbons*.

Davy's researches on flame.—Sir Humphry Davy in 1815 was led to the study of flame by an investigation of the causes and prevention of fire-damp explosions in coal mines, which were prevalent when open candle flames were used. These are caused by the ignition of mixtures of methane (*fire-damp*) and air (or, as we now know, sometimes by the kindling of a mixture of very fine coal-dust with air). Davy soon found that when a flame is cooled it is extinguished, and he recognised that combustible gases have different ignition points.

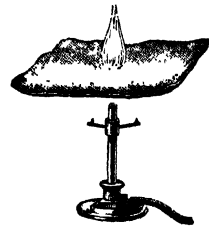


FIG. 334.—Principle of safety lamp.

Lower a close spiral of thick copper wire over a *small* night-light flame : the flame is extinguished.

(i) Depress a piece of fine wire gauze over a Bunsen flame. This does not pass through, owing to cooling by conduction of heat through the metal, and a red-hot ring is seen with a dark centre corresponding with unburnt gas in the centre of the flame. This gas is passing through the gauze, as may be seen by lighting it with a taper. If the gauze remains on the flame, the temperature of the metal rises to the ignition point of the gas, which ignites and burns above the gauze.

(ii) If a piece of gauze, turned up at the edges, is held over an unlighted Bunsen burner, the gas passing through may be kindled above the gauze, but the flame does not pass through. On raising the gauze, the flame flickers and finally goes out (Fig. 334). This flame, in which air is mixed with gas before combustion, is blue and non-luminous.

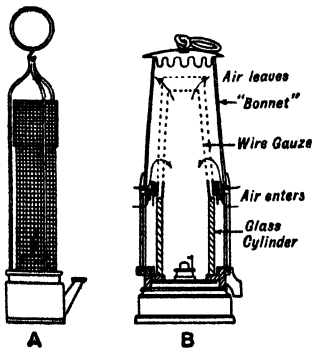


FIG. 335.—Davy's safety lamp.

These experiments led Davy to the invention of the *safety-lamp*, which consists of an oil lamp having a closed cylinder of wire gauze as a chimney (Fig. 335). In its improved form it has a strong glass cylinder below the gauze. Fire-damp will penetrate inside the gauze and burn, but the flame is not propagated outside because the heat is conducted away by the gauze. The gauze may become red-hot, but as the ignition temperature of methane is high, the flame does not pass through. A draught of air blowing on the lamp may cause the gauze

to become so hot as to ignite the fire-damp, and the flame inside may be blown through the gauze by a blast of air faster than 8 ft. per sec., such as is formed on firing a shot. With only a small amount of fire-damp in the air, a flame appears over the flame of the lamp, and from the size of this *flame-cap*, the amount of combustible gas in the air may be judged.

Lower a lighted Davy lamp into a large beaker into which some ether has been poured. The interior of the lamp is filled with flame and it is extinguished, but the ether vapour in the beaker is not ignited.

Davy supposed that the luminosity of a hydrocarbon flame is due to the "decomposition of a part of the gas towards the interior of the flame, where the air was in smallest quantity, and the deposition of solid charcoal, which first by its ignition, and afterwards by its combustion, increases to a high degree the intensity of the light." The non-luminosity of the flame in the second part of the experiment on page 645 was due, according to Davy, to the carbon particles burning as fast as produced in the oxygen supplied.

Flames known to contain solid particles, such as those of zinc, magnesium and potassium burning in oxygen, are very luminous, and the presence of solid particles of carbon in luminous hydrocarbon flames is proved by the fact, observed by Soret (1874), that a beam of sunlight reflected by such a flame is polarised (see p. 4). The presence of carbon particles is also made probable by the following experiments :

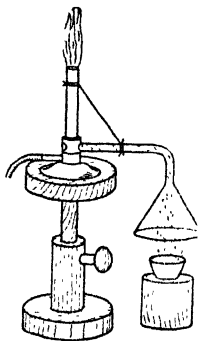


FIG. 336.-- Bunsen flame made luminous by smoke from burning camphor.

Hold a cold piece of pipeclay tube in a candle flame. Carbon is deposited on the lower part only, not on the top.

Clouds of soot evolved from burning camphor, if admitted to the lower part of a Bunsen flame through one air-hole by means of a funnel tube (Fig. 336), render the flame luminous.

Faraday's experiment.—Faraday accepted Davy's views, but instead of supposing that the carbon particles are formed by the decomposition of the gas by heat, he thought they were produced by the preferential combustion of hydrogen in the hydrocarbon, with separation of unburnt carbon which burnt subsequently: $C_2H_4 + O_2 = 2H_2O + 2C$, $2C + 2O_2 = 2CO_2$. Hydrogen was supposed to have a greater affinity for oxygen than has carbon. But Dalton had already shown (p. 607) that if methane or ethylene is exploded with a deficiency of oxygen, all the carbon is burnt to carbon monoxide whilst the whole or part of the hydrogen is set free: $C_2H_4 + O_2 = 2CO + 2H_2$.

The structure of a candle flame is shown by an experiment due to Faraday. A bent glass siphon is lowered into the flame (Fig. 337). With the tube just above the wick, dense white vapours pass into the flask: these

are formed by the vaporisation of wax on the wick. On raising the tube into the bright part of the flame, black vapours pass over, containing particles of carbon. On raising the tube still further, steam and carbon dioxide pass along the siphon.

Frankland's theory.—Sir Edward Frankland in 1861 noticed that the flame of a candle burning on the summit of Mont Blanc gives a feebler light than in the valley at Chamonix, although the rate of combustion was the same in both cases. In further experiments he found that a candle flame burning under a partially exhausted receiver is less luminous than in free air. This had been

noticed by Boyle. An alcohol flame burning in air at 4 atm. pressure is luminous. A mixture of hydrogen and oxygen exploded in a eudiometer burns with a bright flash, and hydrogen burns in oxygen under 20 atm. pressure with a luminous flame. The luminosity of the electric spark in gases increases with the density of the gas. Luminous flames are known in which solid particles cannot be present, *e.g.* flames of phosphorus and arsenic in oxygen, and of sodium in chlorine. Frankland suggested that the luminosity of hydrocarbon flames is due to the presence of *dense gaseous hydrocarbons*, which become incandescent. The presence of solid carbon particles in flames has, however, been proved.

Lewes's theory.—By aspirating and analysing the gas from different parts of the flame, V. B. Lewes in 1892 found that the unsaturated hydrocarbons (ethylene and acetylene) disappear only slowly in the dark portion, but rapidly in the luminous zone. The proportion of acetylene increases rapidly up the dark zone, attaining 70 per cent of the unsaturated hydrocarbons at the apex of the dark cone, although only 1.41 per cent of these hydrocarbons were present. Lewes assumed that hydrocarbons are decomposed by heat, with the intermediate formation of acetylene: $2\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{H}_2 - 2\text{C} + 4\text{H}_2$. Free hydrogen has been detected in the luminous zone. The carbon is separated as a fine powder, and the heat of decomposition of the endothermic acetylene assists in raising the temperature.

The Bunsen flame.—If coal gas is mixed with enough air *before* combustion, as in the familiar Bunsen burner, it burns with a non-luminous flame. This has *two cones*: (1) a pale blue inner cone, which becomes green and smaller when a larger supply of air is admitted and the flame "roars" (as in the Télec burner); (2) a pale blue outer cone, which remains constant in size. The reactions in the inner cone are different from the thermal decompositions taking place in a luminous flame, since partial oxidation now occurs with formation of carbon monoxide and hydrogen, which burn in the outer cone.

The reaction in the bright blue part of a luminous flame (Fig. 333) appears to be the same as that in the inner cone of a Bunsen flame; in

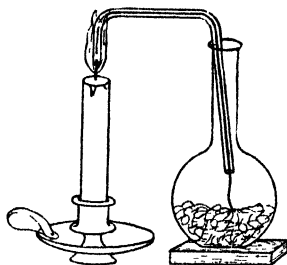


FIG. 337.—Faraday's experiment with a candle flame.

the outer, faintly visible, cone complete combustion of hydrogen and carbon monoxide occurs, as in the outer cone of the Bunsen flame.

The effect of previous admixture of air on the flame may be studied with the apparatus shown in Fig. 338. Undiluted carbon monoxide

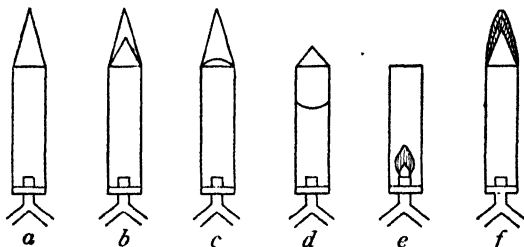


FIG. 338.—Smithells's experiments on flames.

burns above with a hollow cone of blue flame (*a*), typical of what Smithells calls a *volume flame*. If a little air is admitted the cone becomes shorter, and its inner lining bright blue (*b*). With continued addition of air, a mixture is finally produced through which a flame would be propagated without external air, but the flame is kept on the top of the tube by the speed of the gas current (*c*). More air causes the speed of propagation of flame through the mixture to exceed the speed of the gas current, and at this point the inner cone separates from the outer cone in the flame, and passes down the tube (*d*). With more air, the outer cone vanishes, and all the gas now burns in the inner cone (*e*). Now the rate of propagation of flame has been diminished by the excess of air added, and the lower flame is a double cone, as in the first case. When the rate of inflammation has been reduced below the rate of flow of gas, the flame again rises to the top of the tube (*f*), and burns as a single cone with a considerable unburnt inner space, typical of a *surface flame*.

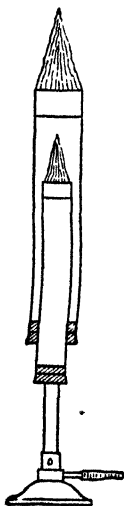


FIG. 339.—Smithells's flame-cone separator.

The separation of the two cones of a Bunsen flame is conveniently made by Smithells's flame-cone separator (1892). This consists (Fig. 339) of one glass tube sliding inside a wider tube, the tubes having metal tops. A mixture of air and coal gas from a Bunsen burner is passed into the central tube. If the quantity of air is increased, the Bunsen flame at the top separates into two cones, one of which remains on the outer tube and the other, the inner cone of the complete flame, passes down and burns on the top of the narrower tube. By raising the latter, the inner cone may be joined to the outer one, and the complete flame raised outside on the inner tube.

The gas from the space between the two cones was found to consist of nitrogen, carbon monoxide, carbon dioxide, steam and hydrogen. The composition of the mixture was the same if pure methane was used.

and the reaction in the inner cone of the Bunsen flame leads to incomplete burning of the hydrocarbon with formation of carbon monoxide and hydrogen, and with excess of oxygen (when some carbon dioxide is formed) an equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ is set up, known as the *water-gas equilibrium*. The law of mass-action :

$$\frac{[\text{CO}] \times [\text{H}_2\text{O}]}{[\text{CO}_2] \times [\text{H}_2]} = K,$$

was shown to hold for the water-gas equilibrium by Horstmann (1877-79), and by Dixon (1884); Smithells and later Haber found that it holds for the interconal gases of a flame, and the constant K has the value corresponding with the temperature of the flame.

The temperatures of flames have been determined in various ways (*e.g.* by platinum and platinum-rhodium thermocouples), and the following values found (Féry, 1904, etc.) :

Bunsen, fully aerated	- 1871°	Hydrogen, free flame	- 1900°
„ insufficient air	- 1812°	Oxy-coal-gas blowpipe	- 2200°
„ acetylene	- 2548°	Oxy-hydrogen blowpipe	- 2420°
„ alcohol	- 1826°	Oxy-acetylene explosion	
Alcohol flame	- 1705°		3000°-4000°

The non-luminosity of the Bunsen flame has been explained as due to :

(1) **Oxidation** : Davy's theory, already considered. That this is only a partial explanation follows from the experiments described below.

(2) **Dilution** : Blochmann found that not only oxygen but also inert gases such as nitrogen, carbon dioxide, or even steam, will render the flame of coal gas non-luminous in the Bunsen burner.

Stop up one air-hole at the base of the burner, and connect the other with an apparatus for generating carbon dioxide. Light the coal gas, and gradually admit carbon dioxide : the flame becomes blue and non-luminous, but consists of only *one* cone instead of two, as in the ordinary Bunsen flame.

Lowe states that 1 volume of ordinary coal gas requires the following volumes of other gases to render it non-luminous : CO_2 , 1.26 ; N_2 , 2.30 ; CO , 5.11 ; H_2 , 12.4 ; air, 2.27 ; O_2 , 0.5. That the effect cannot be due entirely to cooling is evident from the effect of carbon monoxide, which gives a hotter flame than coal gas.

(3) **Cooling** : Wibel showed that cooling a flame causes loss of luminosity.

Bring a cold sand-bath in contact with the flame of coal gas burning at a fishtail burner. The flame loses its luminosity. No soot is deposited.

Suspend a platinum crucible in a Bunsen flame which has been rendered just luminous by adjusting the air-holes when the crucible is red hot. Now pour cold water into the crucible ; the flame loses its luminosity.

If a silica tube is fitted to the top of a Bunsen burner, the flame lighted at the top becomes slightly luminous when the tube is heated to redness by a blowpipe flame. This is not due to chemical change in the gas caused by heating, since Thorpe showed by experiment that this does not occur.

The principle of the stability of the Bunsen flame, viz. that the combustible mixture of gas and air is passed up the tube more rapidly than the flame is propagated down through the mixture, may be illustrated by fitting a long wide glass tube over a large Bunsen burner, and lighting the flame at the top (Fig. 340). On increasing the air supply to the burner, the flame strikes back down the tube.

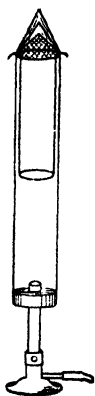


FIG. 340. - Separation of cones of Bunsen flame.

If the air supply is slowly increased, the inner cone of the flame passes down separately, and may be arrested halfway down the tube by a ring of copper wire hung inside, as shown. This prevents the propagation of the flame by cooling the gas below the ignition temperature.

The detonation wave.—By measuring the speed of the mixture of gas and air or oxygen necessary to prevent the downward propagation of a flame in the apparatus described in the above experiment, Bunsen (1867) found that the velocity of propagation of flame in a mixture of hydrogen and oxygen was 34 metres per sec. and much less with other combustible mixtures. Later experiments by Berthelot,

Mallard and Le Chatelier, and Dixon showed that if the explosive mixture is kindled at one end of a long tube, the flame at first traverses a short length of the tube with a velocity comparable with Bunsen's figure, then rapidly increases in speed to a maximum, after which it flashes through the gas with a constant velocity very much higher than the initial velocity of the flame. This flame, travelling with a high constant speed, is called a *detonation wave*. The velocities of the detonation waves in various mixtures, determined by Dixon, are given below in m. per sec.

$8\text{H}_2 + \text{O}_2$	-	3535	$\text{C}_2\text{N}_2 + \text{O}_2$	2728
$2\text{H}_2 + \text{O}_2$	-	2821	$\text{H}_2 + \text{Cl}_2$	1729
$\text{H}_2 + 3\text{O}_2$	-	1712		

In many cases the velocity of the detonation wave is approximately twice that of the propagation of sound through the burnt gas heated to the temperature of combustion under the conditions of experiment.

The increased violence of the combustion and the great speed of the flame in the detonation wave may be shown by the following experiments.

Fill two tubes with nitric oxide over water, one a large test-tube and the other a strong tube 2 in. wide and 5 ft. long, closed at the ends with rubber bungs. Drain any water from the tubes, pour some carbon disulphide into each, and shake. Take out the stoppers, and kindle the gases with a taper. The mixture in each burns with a beautiful blue flame. That in the test-tube burns quietly, but the flame in the long tube runs down noiselessly until it approaches the middle,

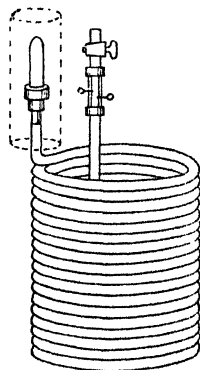


FIG. 341.—Velocity of detonation wave.

and then flashes down quickly, with a peculiar howling noise. In the long tube the detonation wave just begins. A protecting glass screen should be placed before the lower part of the tube.

A coil of lead piping, 30 ft. long and $\frac{1}{4}$ in. diameter, is fitted at each end with the ordinary brass coupling sockets used for gas connections. To one of these is attached by a rubber washer a thin glass test-tube, and to the other, by Faraday's cement, a strong glass tube with firing wires sealed through the glass and a stopcock above (Fig. 341). The coil is filled with a mixture $2\text{CO} + \text{O}_2$, containing a little hydrogen, the test-tube fixed in place, and covered with a wire gauze cylinder. On passing a spark, the test-tube is shattered at the same instant as the flash is seen in the firing tube. The mixture $2\text{CO} + \text{O}_2$ burns in a test-tube without explosion.

CHAPTER XXXIV

BORON AND SILICON

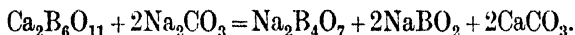
Although boron and silicon belong to two different groups in the Periodic Table, they are very similar in many ways and are conveniently studied together.

BORON.

The salt borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ has been known from early times ; it was brought from Tibet, called *tinca*, and was used as a flux in metallurgy. In 1702 Homberg obtained a crystalline substance *sal sedativum* by distilling green vitriol with borax. Baron (1747) showed that it is an acid, giving borax with soda. It was called *boracic acid* or *boric acid*. Lavoisier suggested that it consists of oxygen united with an unknown radical, later called boron. Davy (1807) first obtained boron as an olive-brown powder by electrolysing moist boric acid, and in 1808 by heating fused boric acid (*i.e.* boron trioxide B_2O_3) with potassium. The preparation by the second method was repeated by Gay-Lussac and Thenard (1808), who described the properties of the element.

Borax.—Most of the borax of commerce is prepared from the natural borax of Searle's Lake, California, and some is made by crystallising the mineral *kernite*, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$. It was formerly made from the minerals *colemanite*, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, and *boracite*, $\text{MgCl}_2 \cdot 2\text{Mg}_3\text{B}_8\text{O}_{15}$ at Stassfurt, and *boronatrocaltite*, $\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$, in Chile.

Powdered colemanite was boiled with sodium carbonate solution and the filtered solution allowed to crystallise :



Borax forms two important hydrates : *octahedral borax* $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ obtained by crystallisation from a hot solution, above 60° , and common *monoclinic borax* $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystallising below 60° . The crystals and powder swell on heating, forming anhydrous borax which melts at 561° , and on cooling forms a transparent glass. Borax is slightly hydrolysed in solution, and since boric acid H_3BO_3 is very weak, the solution is alkaline : $\text{Na}_2\text{B}_4\text{O}_7 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{NaBO}_2 + 2\text{H}_3\text{BO}_3$ (in concentrated solutions) ; $\text{NaBO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{H}_3\text{BO}_3$ (in dilute solutions). Borax is used in laundering to impart a gloss to linen in ironing, in preparing glazes, as a flux in soldering, in making optical and hard glass, and (on account of the properties of boric acid) as an antiseptic. Fused borax dissolves metallic oxides, often producing characteristic colours (*borax-bead reactions* : CuO blue, Cu_2O red, Cr_2O_3 green, MnO_2 violet, CoO deep blue, NiO yellowish-brown, FeO green, Fe_2O_3 , brown).

Boric acid.—Boric acid is made from borax by adding hydrochloric or sulphuric acid to a hot concentrated solution, and it crystallises on cooling: $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} = 2\text{NaCl} + 4\text{H}_3\text{BO}_3$. It is sparingly soluble in cold water, more readily in hot water: 1.95 gm. at 0° , 2.92 gm. at 12° , and 16.82 gm. at 80° , in 100 gm. of water. It is less soluble in solutions of acids.

To a hot saturated solution of borax add concentrated hydrochloric acid till the solution is strongly acid to litmus. On cooling, scaly six-sided crystals of boric acid (Fig. 342) separate. Wash the crystals with cold water and recrystallise from hot water.

In the volcanic regions of Tuscany, jets of steam called *soffioni* escape from the ground. These contain steam, carbon dioxide, hydrogen sulphide, nitrogen, ammonia, and traces of boric acid, which is volatile in steam. The boric acid may have been produced by the action of superheated water on boron nitride: $\text{BN} + 3\text{H}_2\text{O} = \text{H}_3\text{BO}_3 + \text{NH}_3$, or on tourmaline, which contains 3–4 per cent of B_2O_3 and is found *in situ*. In the recovery of the boric acid, the steam is condensed and the liquid is concentrated by the heat of the steam. The crystals of boric acid separating on cooling are recrystallised and dried.

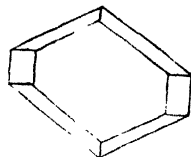


FIG. 342.—Crystal of boric acid.

Ordinary boric acid, or orthoboric acid H_3BO_3 , forms soft, silky, pearly-white triclinic crystals with a greasy feel. At 100° these lose water and form metaboric acid HBO_2 . At 140° pyroboric acid $\text{H}_2\text{B}_4\text{O}_7$ is said to be formed; at a high temperature all the water is lost and boron trioxide B_2O_3 is formed. This softens to a hygroscopic glass at a red heat:



Orthoborates are infrequent: magnesium borate $\text{Mg}_3(\text{BO}_3)_2$ and ethyl borate $\text{B}(\text{OC}_2\text{H}_5)_3$, are best known. Metaborates are the most stable, and pyroborates are also stable. Borax or sodium pyroborate (or diborate, $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$) $\text{Na}_2\text{B}_4\text{O}_7$, is formed by adding a solution of sodium hydroxide or carbonate to boric acid. Metallic borates, usually metaborates, are precipitated by a solution of borax from the metal salts dissolved in water: $\text{Na}_2\text{B}_4\text{O}_7 + \text{BaCl}_2 + 3\text{H}_2\text{O} = \text{Ba}(\text{BO}_2)_2 + 2\text{H}_3\text{BO}_3 + 2\text{NaCl}$. Metaborates are formed in the borax-bead reactions: $\text{Na}_2\text{B}_4\text{O}_7 + \text{CuO} = \text{Cu}(\text{BO}_2)_2 + 2\text{NaBO}_2$.

Boron trioxide shows feebly basic as well as acidic properties. Boric acid combines with sulphur trioxide, forming boron hydrogen sulphate $\text{B}(\text{HSO}_4)_3$, and with phosphoric acid forming boron phosphate BPO_4 , insoluble in water and dilute acids but soluble in alkalis. In this respect boron resembles aluminium.

Boric acid is very weak. It turns litmus a wine-red colour, but has no action on methyl-orange. It is weaker than carbonic acid, or even hydrogen sulphide. The fractions ionised in decinormal solutions at 18° are: carbonic acid ($\text{H} \cdot \text{HCO}_3$), 0.0017; hydrogen sulphide ($\text{H} \cdot \text{HS}$), 0.0007; boric acid ($\text{H} \cdot \text{H}_2\text{BO}_3$), 0.0001.

Boric acid ionises as a monobasic acid and may be titrated with sodium hydroxide after addition of a large amount of glycerol, with phenolphthalein as indicator: $\text{H}_3\text{BO}_3 + \text{NaOH} = \text{NaBO}_2 + 2\text{H}_2\text{O}$. Since the acid has no action on methyl-orange, a solution of borax may be titrated with this indicator as if it were a solution of sodium hydroxide: $\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} = 2\text{NaCl} + 4\text{H}_3\text{BO}_3$.

Boron.—The element boron may be obtained by heating boron trioxide with potassium or sodium: $\text{B}_2\text{O}_3 + 6\text{K} = 2\text{B} + 3\text{K}_2\text{O}$, or potassium fluoborate with potassium: $\text{KBF}_4 + 3\text{K} = 4\text{KF} + \text{B}$. The simplest process is to heat boron trioxide with magnesium: $\text{B}_2\text{O}_3 + 3\text{Mg} = 2\text{B} + 3\text{MgO}$. The chestnut-brown powder left on boiling the mass with dilute hydrochloric acid may be purified by treatment with hydrofluoric acid and fusion with B_2O_3 in a stream of hydrogen (Moissan, 1895).

Heat about 2 gm. of a mixture of 5 gm. of magnesium powder with 15 gm. of powdered boron trioxide in a covered silica crucible. When the violent reaction occurs, cool, and place the crucible in a beaker containing diluted hydrochloric acid (1 : 2). Filter and wash. Dry the boron in a steam oven. Dry potassium fluoborate may be used instead of boron trioxide.

Amorphous boron so prepared is a brown powder, density 2.45; it is unaltered in air at ordinary temperature but smoulders at about 700° , forming the trioxide and some boron nitride BN. These form a superficial coating over the boron and prevent complete reaction. Boron displaces carbon and silicon from their oxides on heating: $3\text{SiO}_2 + 4\text{B} = 2\text{B}_2\text{O}_3 + 3\text{Si}$.

Moissan's boron, prepared as above, always contains oxygen and is said to be a solid solution of a boron suboxide B_4O_3 or B_2O in boron. Weintraub (1909) states that pure boron is insoluble in 40 per cent nitric acid, which dissolves a considerable amount of Moissan's boron, leaving a residue of pure boron. Pure boron is obtained by striking an alternating current arc in a mixture of hydrogen and boron trichloride vapour between water-cooled copper electrodes in a glass globe. The boron powder collecting on the electrodes fuses to globules, which drop off (Pring and Fielding, 1909). As so prepared, boron forms a black, very hard solid with a conchoidal fracture, melting at 2300° , but volatilising appreciably at 1600° . It may be strongly heated in air without oxidation, and is only very slowly attacked by concentrated nitric acid. It thus differs in properties from Moissan's boron. Crystals (plates and needles) of pure boron are deposited on a tantalum wire strongly heated in a mixture of hydrogen and boron tri-bromide vapour (Laubengayer, 1943).

Crystalline boron was obtained by Deville and Wöhler (1857) by fusing boron with aluminium at 1500° . On cooling, crystals form on the surface of the aluminium. The metal may be dissolved in hydrochloric acid, leaving crystals of *adamantine boron*—some clear and colourless, others brown, having the crystalline form of diamond, and very hard and resistant to heat or acids, but dissolving in fused alkalis. The crystals contain about 4 per cent of carbon and up to 7 per cent of aluminium, and are usually regarded as a definite compound, AlB_{12} , or $\text{B}_{48}\text{C}_3\text{Al}_3$. Graphite-like laminae of AlB_2 are also formed,

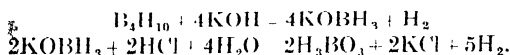
Boron hydrides.—Equal weights of B_2O_3 and magnesium powder on heating form **magnesium boride**, which with acids evolves a gas with a peculiar smell, which burns with a green-edged flame (F. Jones, 1879). Ramsay and Hatfield (1901) showed that the gas contains several hydrides of boron, condensed by liquid air.

The simplest hydride of boron is B_2H_6 , the expected compound BH_3 being unknown. Since B_2H_4 (*diborane*) is decomposed by water, it is not present in the gas from magnesium boride and acid. It is most easily prepared by the action of an electric discharge on a mixture of hydrogen and the vapour of boron trichloride BCl_3 or boron tribromide BBr_3 at low pressure: $2BCl_3 + 5H_2 = B_2H_5Cl + 5HCl$, $6B_2H_5Cl = 5B_2H_6 + 2BCl_3$. With BBr_3 , the hydrogen bromide formed (less volatile) can be separated by fractionation. Diborane is fairly stable in the absence of air, moisture and grease, but slowly decomposes at room temperature to form B_5H_{11} and some $B_{10}H_{14}$, and is rapidly decomposed by water: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$.

The liquid condensed out of the gas from magnesium boride and hydrochloric acid by cooling in liquid air is a mixture of the hydrides B_4H_{10} , B_5H_9 , and B_6H_{10} , separable by fractional distillation, B_4H_{10} being most volatile. At ordinary temperature, these are colourless liquids. Even pure B_4H_{10} rapidly decomposes at ordinary temperature into hydrogen, diborane B_2H_6 , and less volatile hydrides. On heating B_4H_{10} in a sealed tube at 100° , B_2H_6 , B_5H_9 and B_6H_{10} are formed. On heating B_2H_6 , several solid hydrides are formed. One of these, $B_{10}H_{14}$, is volatile *in vacuo*, and soluble in alcohol, ether, or benzene. The properties and sources of the boron hydrides (*boranes*) are summarised below.

	B_2H_6	B_4H_{10}	B_5H_9	B_6H_{10}	$B_{10}H_{14}$	
m.pt. -	165.5°	-120°	-46.6	129°	-65.1° + 99.7°	
b.pt. -	92.5°	+18°	0.66 mm.	0.57 mm.	0°/7 mm. 213°	
	(gas)	----- (liquids) -----				(solid)
Stability -	+	+	+	-	+	
Source -	B_4H_{10}	crude gas	B_4H_{10}	B_2H_6	crude gas	B_2H_6

By the action of B_2H_6 or B_4H_{10} on alkali hydroxide solutions, unstable **hypoborates** are formed, which evolve hydrogen when acidified:



By the action of dry hydrogen chloride on B_2H_6 or B_4H_{10} in presence of aluminium chloride, substitution products are formed:



The action of halogens is violent. With HBr and HI corresponding bromine and iodine compounds are formed.

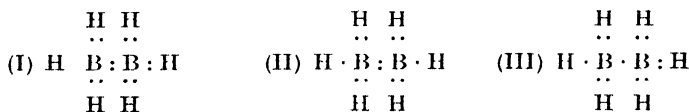
The boranes show some acidic character in reacting with alkali metals and with anhydrous ammonia. B_2H_6 reacts with sodium amalgam to form $[B_2H_6]Na_2$, and B_4H_{10} with sodium to form $[B_4H_{10}]Na_4$. With ammonia the compounds $B_2H_6 \cdot 2NH_3$, $B_4H_{10} \cdot 4NH_3$ and $B_{10}H_{14} \cdot 6NH_3$ are formed; B_5H_{11} reacts as follows: $B_5H_{11} + 4NH_3 = B_5H_9 \cdot 4NH_3 + H_2$. $B_2H_6 \cdot 2NH_3$ is an

electrolyte in liquid ammonia and has been formulated as an ammonium salt $[B_2H_4](NH_4)_2$.

On heating $B_2H_6 \cdot 2NH_3$ or $B_4H_{10} \cdot 4NH_3$, hydrogen is evolved and triborine triamine, $B_3N_3H_6$, is formed: the molecule is a flat hexagonal ring of alternate $-BH-$ and $-NH-$ groups. By the action of dry HCl the three $-BH-$ groups form $-BCl-$.

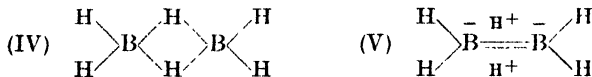
By the action of excess of CO on B_2H_6 under pressure borine carbonyl BH_3CO is formed: $B_2H_6 + 2CO \rightleftharpoons 2BH_3CO$, which reacts with ammonia to form the stable $BH_3CO(NH_3)_2$.

The structure of the boranes is a difficult problem, as they show anomalous valencies. In B_2H_6 the two boron atoms have 6 electrons, and with 6 from the six hydrogens there are only 12 to form seven bonds, leaving two electrons short. It has been suggested that two or more single electron bonds are formed, *e.g.* as in (II) below, but these would confer paramagnetism, which is not found. This has been got over by assuming resonance. Bauer (1937-8) found from electron diffraction that the bonds B—H and B—B are longer than ordinary single covalencies, which indicates some single electron bond or no-electron bond character, so that there may be resonance among arrangements such as:



Wiberg (1936) stressed the feebly acidic properties of the boranes and regarded them as unsaturated polybasic acids, *e.g.* $[B_2H_4]H_2$ or $^+H_2B = ^-BH_2H$ similar to ethylene, etc. In his formulae each boron is surrounded by 8 electrons. The acidic character arises because the B_2H_4 radical, although not electrovalent, can accept protons, and the two protons are inside the electron shell of the B_2H_4 .

Structure (IV) with hydrogen bonds, originally proposed by Dilthey (1921)



and extended by Longuet-Higgins and Bell (1943-6) to other hydrides, is in agreement with physical evidence and resonance theory. Pitzer (1945) regarded the bond between the two boron atoms as a "protonated double bond", composed of a normal covalent double bond with two protons embedded in the electron cloud, the boron atoms having negative charges (V; *cp.* Wiberg's formula).

Halogen compounds of boron.—The following halogen compounds of boron are known:

BF_3 : colourless gas, condensing to colourless, mobile liquid, m. pt. -127° , b. pt. -101° .

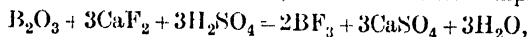
B_2Cl_4 : colourless liquid, b. pt. $0^\circ/40$ mm.

BCl_3 : colourless mobile liquid, m. pt. -107° , b. pt. 12.5° , density 1.431 at 0° .

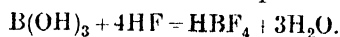
BBr_3 : colourless viscous liquid, m. pt. -46° , b. pt. $90.1^\circ/740$ mm., density 2.650 at 0° .

BI_3 : white leafy crystals, m. pt. 43° , b. pt. 210° .

Boron trifluoride BF_3 is formed by the spontaneous combustion of boron in fluorine. It is prepared by heating a mixture of fluorspar (or potassium fluoborate), boron trioxide, and concentrated sulphuric acid:



or by heating a mixture of boron trioxide and potassium fluoborate at 518° . The gas is collected over mercury. It fumes strongly in moist air, and when passed into water gives a precipitate of boric acid, which redissolves if more gas is passed in, and the solution then contains fluoboric acid: $4BF_3 + 3H_2O = B(OH)_3 + 3HBF_4$. This is more easily made by dissolving boric acid in cooled 50 per cent hydrofluoric acid:



The solution on distillation gives a strongly acid liquid of composition $BF_3 \cdot 2H_2O$; in concentrated solutions BF_3 and HF are present. The acid forms salts, called fluoborates, e.g. KBF_4 is thrown down as an amorphous white precipitate on addition of a potassium salt to the acid. BF_3 readily combines with ammonia, giving a white solid, $BF_3 \cdot NH_3$. Fluoborates are formed in solution from boric acid and acid fluorides: $H_3BO_3 + 2NaHF_2 = NaBF_4 \cdot NaOH + 2H_2O$. They are decomposed by heat: $KBF_4 = KF + BF_3$. The acids $HClO_4$ and HF_4 show similarities, especially in the capacity to form salts with organic bases.

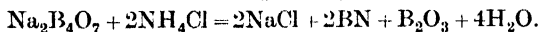
Boron trichloride BCl_3 is obtained by burning amorphous boron in chlorine, by heating B_2O_3 with phosphorous pentachloride in a sealed tube at 150° : $B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3$, or by passing dry chlorine over a strongly-heated mixture of boron trioxide and charcoal: $B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$. It is condensed in a freezing mixture. The liquid is freed from chlorine by distillation over mercury. It fumes strongly in moist air, and is irreversibly hydrolysed by water: $BCl_3 + 3H_2O = B(OH)_3 + 3HCl$.

Boron dichloride B_2Cl_4 is formed in small yield by striking an arc with a zinc anode in liquid BCl_3 . It reacts with water to form an oxide B_2O_2 , and evolves hydrogen with alkalis:



Boron tribromide BBr_3 is obtained by similar methods to the chloride. Boron tri-iodide BI_3 is formed by passing BCl_3 vapour and HI through a heated tube. It burns when heated in oxygen.

Boron nitride.—Boron is one of the elements which combine directly with nitrogen (p. 512): the nitride is usually prepared by heating borax with ammonium chloride, extracting with hydrochloric acid, and washing:

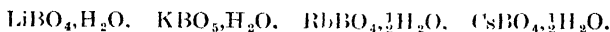


Boron burns when heated in nitric oxide: $5B + 3NO = B_2O_3 + 3BN$. Boron nitride BN is a white infusible powder, unchanged by mineral acids, solutions of alkalis, or chlorine at a red heat. It is decomposed by fusion with potash, when heated in steam: $2BN + 3H_2O = B_2O_3 +$

2NH_3 , or (slowly) by hydrofluoric acid : $\text{BN} + 4\text{HF} = \text{NH}_4\text{BF}_4$. When fused with potassium carbonate, it forms potassium cyanate : $\text{BN} + \text{K}_2\text{CO}_3 = \text{KBO}_2 + \text{KCNO}$.

Boron forms a carbide B_4C on heating with carbon in the electric furnace, and a sulphide B_2S_3 by direct combination at a white heat, or by heating B_2O_3 with carbon in the vapour of CS_2 . The sulphide is hydrolysed by water : $\text{B}_2\text{S}_3 + 6\text{H}_2\text{O} = 2\text{H}_3\text{BO}_3 + 3\text{H}_2\text{S}$. B_2S_3 is said by Moissan to be formed from BI_3 and S dissolved in CS_2 . **Metathioboric acid** HBS_2 is formed in white needles by the action of H_2S on BBr_3 .

Perborates.—Sodium perborate $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (formerly regarded as a metaborate containing hydrogen peroxide of crystallisation, $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$) is a crystalline solid obtained by the action of hydrogen peroxide and sodium hydroxide, or of sodium peroxide, on cooled borax solution ; or by the electrolysis of a solution of borax and sodium carbonate with a platinum gauze anode. It is stable and only sparingly soluble and is used as a bleaching and disinfecting agent. The solution is stable at room temperature but evolves oxygen on warming ; it does not liberate iodine from concentrated potassium iodide solution. Other perborates are :



They are prepared by the action of concentrated hydrogen peroxide on metaborates and evaporation under reduced pressure or precipitation by alcohol.

Tests for boric acid.—If a solution of a borate is acidified with hydrochloric acid and a piece of turmeric paper dipped into the solution and dried, a brownish-red colour is produced, similar to that formed by alkalis. If the paper is now moistened with alkali, it turns greenish-black. When a mixture of a borate, powdered fluorspar, and concentrated sulphuric acid is held on a platinum wire in a Bunsen flame, the boron fluoride formed colours the flame green.

Ethyl borate $\text{B}(\text{OC}_2\text{H}_5)_3$ is formed when a borate is distilled with alcohol and concentrated sulphuric acid : $\text{B}(\text{OH})_3 + 3\text{C}_2\text{H}_5\text{OH} = \text{B}(\text{OC}_2\text{H}_5)_3 + 3\text{H}_2\text{O}$. The vapour burns with a green flame.

Add a little borax and concentrated sulphuric acid to alcohol in a dish. Stir well and ignite. The flame is tinged green, especially if blown out and rekindled. Since copper and barium salts also colour the flame green, the test is best made by heating the mixture in a small flask fitted with a glass jet (Fig. 343), and burning the vapour after admixture with air in a wider tube to destroy the luminosity of the flame (due to ether, $(\text{C}_2\text{H}_5)_2\text{O}$, also formed).

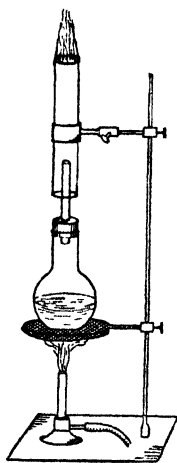


FIG. 343.—Green flame of ethyl borate.

Since boric acid interferes in qualitative analysis with the group separation of the metals, it is removed by repeated evaporation of the solution with hydrochloric acid. The boric acid is volatile in steam and

is slowly but completely eliminated. If the acid is not removed, insoluble borates *e.g.* calcium borate $\text{Ca}(\text{BO}_2)_2$, are precipitated by ammonia in Group III.

SILICON.

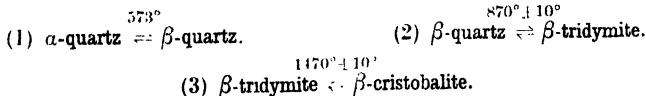
Next to oxygen, silicon is the most abundant element in the crust of the earth: it occurs as **silicon dioxide** or *silica*, SiO_2 , varieties of which are quartz, sand, flint, etc. Silica is also the acidic constituent of the silicate rocks. Granite and similar primitive rocks contain from 20 to 30 per cent of silicon. Silica was at first regarded as an "earth," analogous to lime and alumina, but its acidic character was pointed out by Otto Tachenius in 1666: it is insoluble in acids but dissolves in potash, forming a solution of a silicate formerly called *liquor of flints*. Tachenius also observed that acids differ in strength; one acid is displaced from its compounds by a stronger acid.

Gay-Lussac and Thenard in 1811 obtained silicon as a brown powder on passing silicon fluoride gas over heated potassium, but they did not recognise its true character. In 1823 Berzelius prepared silicon by heating potassium fluosilicate with potassium: $\text{K}_2\text{SiF}_6 + 4\text{K} = 6\text{KF} + \text{Si}$. In most of its properties silicon belongs to the group of non-metals, although it forms alloys with copper and iron. It differs from carbon by giving a solid, difficultly-fusible dioxide SiO_2 , which is the chemical analogue of carbon dioxide CO_2 .

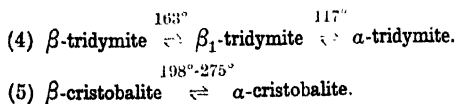
The great difference between silica and carbon dioxide is due rather to a peculiarity of silica. According to G. N. Lewis the structure of silica should be represented as a "giant molecule":

In gaseous and solid carbon dioxide the separate molecules $\text{O}=\text{C}=\text{O}$ are present, whilst silica consists of tetrahedral SiO_4 groups linked together by strong bonds. The arrangement of the atoms in the different forms of silica is different, but they all contain SiO_4 groups. These are linked so that every oxygen atom is shared by two tetrahedra, giving the composition SiO_2 .

The forms of silica.—Silica occurs both *crystallised* and *amorphous*. The three main crystalline forms are *quartz*, *tridymite* and *cristobalite*, although different modifications of each exist, having definite transition points (Fenner, 1912-14).



β -tridymite and β -cristobalite pass at the following temperatures into metastable modifications with lower optical symmetry:



The relations among the forms is shown *diagrammatically* in Fig. 344. Quartz is the only *stable* form below 870°; the three tridymites and β -cristobalite can exist below 870° but are metastable. The transitions (1), (4) and (5) above occur rapidly, but (2) and (3), as well as the transition β -cristobalite \rightleftharpoons liquid at about 1710°, are sluggish. Between 870° and 1470°, β -tridymite is the stable form; from 1470° to 1710°, β -cristobalite.

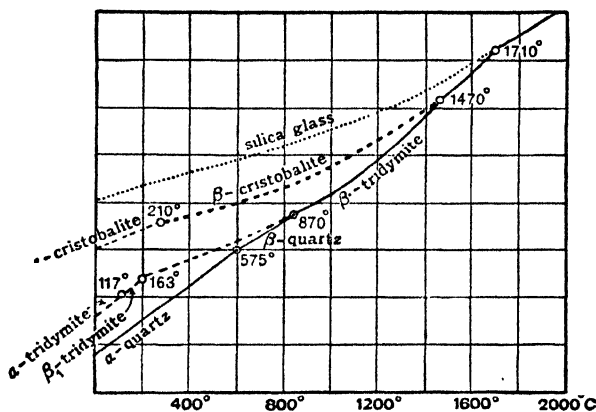


FIG. 344.—Forms of Silica.

Silica glass, formed by rapid cooling of the liquid, can exist from ordinary temperature to 1000° or above, when it begins to crystallise, this taking place at an appreciable rate above 1250°. In devitrifying it always forms cristobalite, even at temperatures below the cristobalite range, unless a flux is present. This is an example of a general rule, pointed out by Ostwald, that metastable states tend to be formed first. Cristobalite tends to change into tridymite rather than quartz; the direct transformation of quartz into tridymite, without a flux, is doubtful.

Since quartz changes into cristobalite (or tridymite) with expansion, silica bricks are liable to shatter when quickly heated unless a large proportion of the quartz has been converted into the form stable at high temperatures by previous heat treatment: this form remains metastable on cooling.

Silica also occurs in vegetable and animal organisms. The straw of cereals and bamboo cane contain fairly large quantities, and the weed "horse-tail" on combustion leaves a siliceous skeleton. The feathers of some birds contain 40 per cent of silica, which also occurs in sponges, and deposits of almost pure silica are found as *kieselguhr*, which consists of the siliceous skeletons of extinct diatoms. This material, being very porous, is used to absorb nitroglycerin in the preparation of dynamite, and in lagging steam pipes to retard loss of heat.

Superheated water in the interior of the earth, especially if alkaline, dissolves silica, which occurs in many spring waters, in hot-springs (Black, 1794), and particularly in the boiling water of geysers. The silica is

deposited at the mouth of the geyser as *sinter*. Silica may pass into the pores of wood, etc., in the earth, producing *petrifaction*.

Quartz.—Quartz (density 2.648) occurs as *rock-crystal* in clear colourless crystals used for optical apparatus, but more often in opaque (“milky”) or coloured masses (“smoky-quartz,” “cairngorm”). Coloured varieties (e.g. purple, in *amethysts*) are used as gems. *Sand* consists of quartz which remains unchanged after the disintegration or “weathering” of rocks, and has been crushed during its movement by water. The purest sand (“Calais sand”) is white; yellow sand is coloured by ferric oxide, dissolved by boiling hydrochloric acid.

“Singing sand,” which emits a peculiar squeaking note when pressed, consists of rounded grains of nearly uniform size. It occurs in patches with ordinary sand e.g. near Poole.

The crystalline form of quartz is complicated; it is apparently a hexagonal prism, terminated by a hexagonal pyramid, but the crystal is really a tetartohedral trigonal trapezohedron with lower symmetry, and has optical activity. Some crystals have hemihedral facets inclined to the right, others to the left, so that one type of crystal is the mirror-image of the other (Fig. 345). Such pairs of crystals are known as **enantiomorphs**.

If hydrated silica (p. 662) is heated with a solution of soluble glass (sodium silicate) in a sealed tube, small crystals of quartz are formed. Larger crystals are formed by prolonged heating at 250° in a sealed tube of a 10 per cent solution of colloidal silica. Spezia (1905-9) obtained quartz crystals more than 1 cm. long from solutions of quartz in sodium silicate and sodium chloride kept for some months at 330°.

Tridymite.—Tridymite (density 2.26) occurs more rarely than quartz in minute crystals, usually six-sided plates (Fig. 346) in cavities in the trachytic rocks of Mexico and Stenzelberg and in solidified magmas and lavas. It belongs to the hexagonal system.

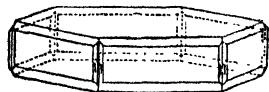


FIG. 346.—Crystalline form of tridymite.

Amorphous silica.—All varieties of silica soften below 1600°, melt in the oxyhydrogen blowpipe at about 1710° and boil in the electric furnace at 2230°. Before fusion they become plastic and can be blown like glass, or drawn into thread. The amorphous *silica glass*, density 2.2, first made by Gaudin in 1839, has a very small coefficient of ex-

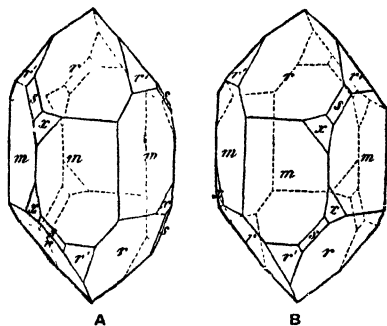


FIG. 345.—Enantiomorphous crystals of quartz; A left-handed, B right-handed, crystal.

Cristobalite.—This is a cubic crystalline form (density 2.32) found in some volcanic rocks and in meteorites. It is formed by heating powdered silica glass at 1500°.

with hydrofluoric and sulphuric acids to remove silica. It has a purity of 96–97 per cent.

The so-called *amorphous silicon* so prepared is a light chestnut-brown hygroscopic powder, density 2.35, which burns brilliantly when heated to dull redness in oxygen. The X-rays show that it really contains minute octahedral crystals, and all the known forms of silicon are octahedral. When heated in air it burns superficially. It ignites spontaneously in fluorine, forming the fluoride SiF_4 , and burns when heated in chlorine with production of the tetrachloride SiCl_4 . It is insoluble in water and all acids except a mixture of nitric and hydrofluoric: it is slowly attacked by steam at a red heat: $\text{Si} + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2$. A mixture of potassium chlorate and nitric acid has no action upon it (*cf.* carbon), but it dissolves readily in concentrated alkali hydroxides: $\text{Si} + 2\text{KOH} + \text{H}_2\text{O} = \text{K}_2\text{SiO}_3 + 2\text{H}_2$, or in fused sodium carbonate, and burns brilliantly in fused potassium nitrate, or potassium chlorate.

Amorphous silicon strongly heated in a closed crucible fuses, and on cooling solidifies to the dense crystalline *graphitoidal silicon*, also formed by the reduction of silica in the electric furnace. Octahedral crystals of silicon, orange or black in colour, are produced by strongly heating potassium fluosilicate with sodium and zinc, or with aluminium in an iron crucible, and treating the mass with acid: $3\text{K}_2\text{SiF}_6 + 4\text{Al} = 4\text{AlF}_3 + 3\text{Si} + 6\text{KF}$. Zinc gives long needle-shaped crystals of *adamantine silicon*, aluminium six-sided plates of graphitoidal silicon; both varieties are made up of regular octahedra. Crystalline silicon scratches glass: it has a density of 2.49; it does not burn in oxygen even when strongly heated, but burns when heated in chlorine, and ignites spontaneously in fluorine. When very strongly heated, it forms grey nodules. It is attacked by a mixture of nitric and hydrofluoric acids, or by fusion with alkali: when fused with sodium carbonate it displaces carbon: $\text{Si} + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SiO}_3 + \text{C}$. Another variety (density 2.42) is formed on crystallising from molten silver.

Silicon hydrides.—If a mixture of 2 parts of magnesium powder and 1 part of *dry* amorphous silica is heated in a crucible a violent reaction occurs and **magnesium silicide**, mainly Mg_2Si , is formed as a bluish crystalline mass. This when treated with dilute hydrochloric acid in a flask from which air has been displaced by hydrogen, evolves a spontaneously inflammable gaseous mixture of silicon hydrides with hydrogen: $\text{Mg}_2\text{Si} + 4\text{HCl} = 2\text{MgCl}_2 + \text{SiH}_4$ (Wöhler, 1858). If the gas is bubbled through water, each bubble ignites in contact with the air and burns with a luminous flame, producing a vortex ring of finely-divided silica: $\text{SiH}_4 + 2\text{O}_2 = \text{SiO}_2 + 2\text{H}_2\text{O}$ (*cf.* phosphine).

If the gas is washed with water and dried with calcium chloride and phosphorus pentoxide, and then passed through a tube cooled in liquid air, a liquid mixture of silicon hydrides is condensed, from which the following compounds may be isolated by fractionation:

1. **Monosilane** SiH_4 , m. pt. -185° , b. pt. -112° , a colourless gas stable at the ordinary temperature, spontaneously inflammable if mixed with the other hydrides and sometimes if pure; relative density 16.02 ($\text{H} = 1$);

decomposed when passed through a red-hot tube, to twice its volume of hydrogen: $\text{SiH}_4 = \text{Si} + 2\text{H}_2$. By the action of alkalis, four times the volume of hydrogen is produced: $\text{SiH}_4 + 2\text{KOH} + \text{H}_2\text{O} = \text{K}_2\text{SiO}_3 + 4\text{H}_2$. The gas precipitates copper silicide Cu_2Si from copper salts, and silver from silver salts: $4\text{AgNO}_3 + \text{SiH}_4 = \text{Si} + 4\text{Ag} + 4\text{HNO}_3$.

Pure monosilane is obtained by heating triethyl silico formate (see p. 667) with sodium: $4\text{SiH}(\text{OC}_2\text{H}_5)_3 = \text{SiH}_4 + 3\text{Si}(\text{OC}_2\text{H}_5)_4$ (ethyl ortho-silicate).

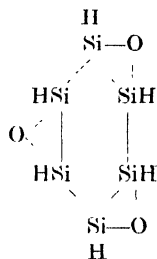
2. **Disilane** Si_2H_6 , a colourless gas, b. pt. -14.5° , m. pt. 132.5° , stable at the ordinary temperature but rapidly decomposed at 300° ; relative density 31.7 (H = 1); inflames in the air; soluble in benzene and carbon disulphide; decomposed by alkalis: $\text{Si}_2\text{H}_6 + 2\text{H}_2\text{O} + 4\text{KOH} = 2\text{K}_2\text{SiO}_3 + 7\text{H}_2$.

3. **Trisilane** Si_3H_8 , a colourless liquid, b. pt. 53° , m. pt. -117° , decomposing spontaneously at the ordinary temperature. Si_3H_8 and Si_2H_6 react vigorously with carbon tetrachloride and chloroform: $2\text{CCl}_4 + \text{Si}_2\text{H}_6 = 2\text{SiCl}_4 + 2\text{C} + 3\text{H}_2$.

4. **Tetrasilane** Si_4H_{10} , b. pt. 109° , m. pt. -90° , less stable than Si_3H_8 .

5. **Solid hydrides**, probably Si_5H_{12} and Si_6H_{14} , remain after fractionation. Brown solid **silicon dihydride** $(\text{SiH}_2)_x$ is obtained by the action of glacial acetic acid or a solution of HCl in alcohol on CaSi (prepared by heating Ca and Si at 1050°) (Schwarz and Heinrich, 1935). No gaseous unsaturated hydrides corresponding with ethylene, etc., are known.

By the action of dilute alcoholic hydrogen chloride on CaSi_2 , Kautsky (1921-23) obtained white crystalline **siloxene** $\text{Si}_6\text{O}_3\text{H}_6$:



Siloxene inflames spontaneously in air and decomposes water. By the action of bromine on siloxene under carbon disulphide, yellow **silical bromide** $\text{Si}_6\text{O}_3\text{Br}_6$ is formed, which is hydrolysed by water into black **silical hydroxide** $\text{Si}_6\text{O}_3(\text{OH})_6$ a base giving coloured salts.

From SiH_4 and dry hydrogen chloride in presence of aluminium chloride the substitution products SiH_3Cl , m. pt. -118° , b. pt. 3.05° , and SiH_2Cl_2 , m. pt. -122° , b. pt. 8.5° , are formed: $\text{SiH}_4 + \text{HCl} = \text{SiH}_3\text{Cl} + \text{H}_2$. From SiH_4 and solid bromine at 80° , SiH_3Br , m. pt. 94° , b. pt. 1.9° , and SiH_2Br_2 , m. pt. -70.1° , b. pt. 66° , are formed. By the action of water on SiH_3Br a colourless, odourless, combustible gas, **disiloxane** $(\text{SiH}_3)_2\text{O}$, m. pt. -144° , b. pt. -15.2° , is produced: $2\text{SiH}_3\text{Br} + \text{H}_2\text{O} = (\text{SiH}_3)_2\text{O} + 2\text{HBr}$. SiH_2Br_2 gives **prosiloxane** SiH_2O , which rapidly polymerises: $\text{SiH}_2\text{Br}_2 + \text{H}_2\text{O} = \text{SiH}_2\text{O} + 2\text{HBr}$.

Halogen compounds of silicon.—Compounds of silicon with all the halogens of the types SiX_4 and SiHX_3 , are known; isolated compounds of the types SiH_2X_2 and SiH_3X have been prepared, and several chlorides not corresponding with the type SiX_4 are known.

Silicon tetrachloride (Berzelius, 1823) is produced when amorphous silicon, or the mixture of this with magnesia obtained by heating 40 gm. of dry powdered sand with 10 gm. of magnesium powder, is heated in a current of dry chlorine: $\text{Si} + 2\text{Cl}_2 = \text{SiCl}_4$. Chlorine may also be

passed over heated silicon-iron. An older method of preparation is to heat an intimate mixture of silica and carbon in a porcelain tube in a stream of dry chlorine: $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 = \text{SiCl}_4 + 2\text{CO}$. The products of reaction are cooled in a worm-tube, when silicon tetrachloride condenses as a colourless volatile liquid, density 1.50 at 0° , m. pt. -70° , b. pt. 56.8° , which fumes strongly in moist air owing to hydrolysis: $\text{SiCl}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{HCl}$. It forms dense fumes with ammonia. Silicon tetrachloride is also obtained when carbon tetrachloride vapour is passed over heated silica: $\text{SiO}_2 + \text{CCl}_4 = \text{SiCl}_4 + \text{CO}_2$.

By the action of chlorine on heated silicon, silicon trichloride Si_2Cl_6 (m. pt. -1° , b. pt. 145°) and silicon octachloride Si_2Cl_8 (b. pt. 210° - 215°) are also formed. These may be separated by fractionation. The trichloride is also produced when the vapour of the tetrachloride is passed over strongly-heated silicon. It is a colourless fuming liquid, the hot vapour of which ignites spontaneously in air. With water it forms an explosive white solid, $\text{Si}_2\text{H}_2\text{O}_4$ or $(\text{SiO}\cdot\text{OH})_2$, silicon-oxalic acid: $\text{Si}_2\text{Cl}_6 + 4\text{H}_2\text{O} = (\text{SiO}_2\text{H})_2 + 6\text{HCl}$. The octachloride with water forms a white powder of silicon-mesoxalic acid $\text{H}_2\text{Si}_2\text{O}_5$, the structural formula of which has been given as $\text{SiO}_2\text{H}\cdot\text{SiO}\cdot\text{SiO}_2\text{H}$. The compounds $\text{Si}_4\text{Cl}_{10}$, $\text{Si}_5\text{Cl}_{12}$ and $\text{Si}_6\text{Cl}_{14}$ have been described.

The silicon bromides SiBr_4 (b. pt. 153°) and Si_2Br_6 (solid) are formed in the same way as SiCl_4 , and by the action of bromine on Si_2I_6 , respectively. Si_3Br_8 and $\text{Si}_4\text{Br}_{10}$ are formed by the action of the silent discharge on silicon bromoform, SiHBr_3 .

Silicon tetraiodide SiI_4 (m. pt. 120.5°) is formed from iodine vapour and heated silicon. When heated with finely-divided silver at 280° , it forms silicon tri-iodide: $2\text{SiI}_4 + 2\text{Ag} = 2\text{AgI} + \text{Si}_2\text{I}_6$. The tri-iodide forms splendid crystals, fuming in moist air.

Several silicon oxychlorides are described: Si_2OCl_6 (b. pt. 137°), $(\text{SiOCl}_2)_4$ (m. pt. 77°), $\text{Si}_4\text{O}_3\text{Cl}_{10}$, $\text{Si}_5\text{O}_4\text{Cl}_{12}$, $\text{Si}_6\text{O}_5\text{Cl}_{14}$, $\text{Si}_7\text{O}_6\text{Cl}_{16}$ (all liquids), separable by fractionation.

Silicon chloroform SiHCl_3 , b. pt. 32° , m. pt. -134° , sp. gr. (15°) 1.3438, discovered by Buff and Wöhler (1857), is prepared by passing hydrogen chloride over silicon (or the mixture of silicon and magnesia, p. 663) at a dull red heat: $\text{Si} + 3\text{HCl} = \text{SiHCl}_3 + \text{H}_2$. The liquid condensed in a freezing mixture is fractionated to separate silicon tetrachloride (b. pt. 56.8°) also produced. Silicon chloroform is a colourless, mobile, fuming liquid, which is very inflammable and burns with a green-edged flame, emitting white fumes of silica. A mixture of the vapour with air or oxygen explodes when brought in contact with a flame. At 800° the vapour decomposes into Si, H_2 , HCl, SiCl_4 , and a trace of less volatile liquid: $4\text{SiHCl}_3 = \text{Si} + 2\text{H}_2 + 3\text{SiCl}_4$.

The action of ice-cold water on silicon chloroform forms silicoformic anhydride $\text{H}_2\text{Si}_2\text{O}_3$, a white solid, probably polymerised $[\text{SiH}(\text{O})_2]_n\text{O}$. This is a powerful reducing agent: $\text{H}_2\text{Si}_2\text{O}_3 + \text{O}_2 = 2\text{SiO}_2 + \text{H}_2\text{O}$ (cf. formic acid, $\text{H}\cdot\text{CO}_2\text{H} + \text{O} = \text{CO}_2 + \text{H}_2\text{O}$). It is readily decomposed by dilute alkalis with evolution of hydrogen: $\text{H}_2\text{Si}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{SiO}_2 + 2\text{H}_2$. On heating, silicoformic anhydride decomposes ultimately into silica, silicon, and hydrogen: $2\text{H}_2\text{Si}_2\text{O}_3 = \text{SiH}_4 + 3\text{SiO}_2 = \text{Si} + 2\text{H}_2 + 3\text{SiO}_2$. By the action of silicon

chloroform on methyl alcohol or sodium methoxide, methyl silicoformate $\text{SiH}(\text{OCH}_3)_3$, b. pt. $104^\circ-6''$ is formed. With ethyl alcohol or sodium ethoxide, ethyl silicoformate $\text{SiH}(\text{OC}_2\text{H}_5)_3$ is obtained: $\text{SiHCl}_3 + 3\text{NaOC}_2\text{H}_5 = \text{SiH}(\text{OC}_2\text{H}_5)_3 + 3\text{NaCl}$. These compounds are analogous to orthoformic esters, e.g. $\text{CH}(\text{OC}_2\text{H}_5)_3$.

Silicon bromoform SiHBr_3 (b. pt. $116'$, m. pt. -100°) is produced by the action of hydrogen bromide in heated silicon; **silicon iodoform** SiHI_3 (m. pt. $8''$, b. pt. c. $220'$) is formed by the action of a mixture of hydrogen iodide and iodine on heated silicon. Numerous mixed halogen compounds of silicon, e.g. SiCl_3Br , are described.

Silicon fluoride.— Amorphous and crystalline silicon ignite spontaneously in fluorine, forming gaseous silicon fluoride SiF_4 . Pure silicon fluoride is obtained by heating barium fluosilicate: $\text{Ba}_2\text{SiF}_6 = \text{BaF}_2 + \text{SiF}_4$. Silicon fluoride is more conveniently prepared by the action of hydrofluoric acid on silica (Scheele, 1771): $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$. Since it is decomposed by water, some dehydrating agent is added. Usually a mixture of equal weights of powdered fluorspar and white sand is heated in a thick glass flask with three times its weight of concentrated sulphuric acid: $2\text{CaF}_2 + 2\text{H}_2\text{SO}_4 + \text{SiO}_2 = 2\text{CaSO}_4 + \text{SiF}_4 + 2\text{H}_2\text{O}$. The colourless gas, which fumes strongly in moist air, is collected over mercury. To free it from hydrogen fluoride, it may be passed over sodium fluoride. Silicates and glass are decomposed by hydrofluoric acid, with formation of silicon fluoride.

Silicon fluoride is a colourless, incombustible, strongly fuming gas, normal density 4.684 gm./lit. It solidifies without previous liquefaction at $97'$ under atmospheric pressure. The solid melts at -77° under 2 atm. pressure, and the liquid boils at -65° under 941 mm. pressure. Silicon fluoride extinguishes a burning taper, but potassium and sodium burn in it when heated: $4\text{K} + 2\text{SiF}_4 = \text{K}_2\text{SiF}_6 + 2\text{KF} + \text{Si}$, and heated calcium and barium oxides react with incandescence: $\text{SiF}_4 + 2\text{CaO} = 2\text{CaF}_2 + \text{SiO}_2$.

Silicon fluoroform SiHF_3 , analogous to silicon chloroform, is obtained from this by the action of stannic fluoride or titanium tetrafluoride: $4\text{SiHCl}_3 + 3\text{SnF}_4 = 4\text{SiHF}_3 + 3\text{SnCl}_4$. It is a combustible gas, b. pt. $80.2''$, m. pt.

$110'$, which decomposes on heating: $4\text{SiHF}_3 = 3\text{SiF}_4 + 2\text{H}_2 + \text{Si}$, and in contact with water: $2\text{SiHF}_3 + 2\text{H}_2\text{O} = \text{SiO}_2 + \text{H}_2\text{SiF}_6 + 2\text{H}_2$.

Silicon trifluoride Si_2F_6 is a colourless inflammable gas, obtained by the action of zinc fluoride on silicon trichloride: $\text{Si}_2\text{Cl}_6 + 3\text{ZnF}_2 = \text{Si}_2\text{F}_6 + 3\text{ZnCl}_2$. It is decomposed by water: $\text{Si}_2\text{F}_6 + 2\text{H}_2\text{O} = \text{SiO}_2 + \text{H}_2\text{SiF}_6 + \text{H}_2$ (Schumb and Gamble, 1932).

Hydrofluosilicic acid.— The reaction between silicon fluoride and water was discovered by Scheele in 1771 but was only completely explained by Berzelius in 1823. It gives gelatinous silica and soluble hydrofluosilicic acid H_2SiF_6 : $3\text{SiF}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2\text{SiF}_6$. If hydrofluoric acid is added until the silica is just dissolved, more hydrofluosilicic acid is formed, and the difficult filtration is avoided: $\text{SiO}_2 + 6\text{HF} = \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$. The acid is made on the large scale (for lead refining, *q.v.*) by percolating aqueous hydrofluoric acid through sand.

Heat a mixture of 50 gm. of powdered fluorspar, 50 gm. of fine white sand, and 200 ml. of concentrated sulphuric acid in a stout glass flask (thin glass is soon perforated) on a sand-bath, and pass the silicon fluoride (fuming in air) into a cylinder, the dry delivery tube dipping under mercury

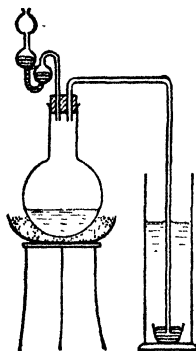


FIG. 347.—Preparation of hydrofluosilicic acid.

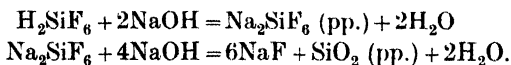
in a small crucible over which water is afterwards poured. This is to prevent the tube becoming choked by the gelatinous silica (Fig. 347). The silica is deposited in small sacs, each enclosing a bubble of gas; these should be broken occasionally by stirring with a glass rod. The liquid is filtered through linen, and the silica when washed, dried, and heated, is very pure (sp. gr. 2.2).

A concentrated solution of hydrofluosilicic acid fumes in the air. The anhydrous acid is not known and silicon fluoride and dry hydrogen fluoride do not react.

Hydrofluosilicic acid is obtained as a by-product in the manufacture of superphosphate by treating minerals containing *apatite* with sulphuric acid (p. 759).

Pure hydrofluosilicic acid does not corrode glass, but on evaporation it decomposes: $\text{H}_2\text{SiF}_6 = \text{SiF}_4 + 2\text{HF}$, and the hydrofluoric acid formed corrodes a flask or porcelain basin. With steam at high temperatures, crystals of silica are formed.

When hydrofluosilicic acid solution is titrated with alkali the following reactions occur:



The end-point, with phenolphthalein, is therefore reached when six molecules of base have been added per molecule of acid.

Salts of hydrofluosilicic acid, *fluosilicates*, are prepared by the action of gaseous silicon fluoride on the solid fluorides: $\text{SiF}_4 + 2\text{NaF} = \text{Na}_2\text{SiF}_6$. The following are sparingly soluble and are precipitated when hydrofluosilicic acid is added to solutions of salts of the metals: Na_2SiF_6 , K_2SiF_6 , BaSiF_6 , rare earth salts. The salts K_2SiF_6 and Na_2SiF_6 are formed as nearly transparent gelatinous precipitates; BaSiF_6 forms a white crystalline precipitate; calcium and strontium salts are not precipitated. The lithium salt Li_2SiF_6 is soluble and precipitates Na_2SiF_6 with sodium chloride.

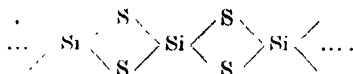
Silicon carbide.—If a mixture of 5 parts of sand and 3 parts of crushed coke with a little salt and sawdust, is heated electrically to 1550° – 2200° by a carbon rod passing through the mass (*cf.* graphite), silicon carbide SiC is formed: $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$. This compound, discovered by Acheson in 1891, is manufactured in large quantities for use as an abrasive instead of emery, since it is nearly as hard as diamond. The technical product is a black, coarsely-crystallised mass with a play of iridescent colours. It is infusible and may be used in furnace-linings; it resists most reagents but fused sodium hydroxide exposed to air

slowly acts upon it: $\text{SiC} + 4\text{NaOH} + 2\text{O}_2 = \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O}$. Pure silicon carbide forms transparent, colourless or green, six-sided plates, density 3.1, and is obtained by fusing silicon with carbon in the electric furnace.

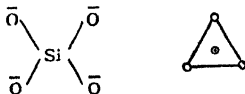
Silicon carbide has the same lattice as diamond in which half the carbon atoms are replaced by silicon. The silicon carbide in the electric furnace is surrounded by a layer of *Siloxicon*, which is said to be a definite compound Si_2OC_2 mixed with a little silicon monoxide SiO , but it may be a solid solution of silica in silicon carbide. It is used as a refractory. A fibrous variety called *Fibrox* is used as a heat insulator instead of asbestos.

Silicon borides SiB_3 and SiB_6 , very hard, are formed in the electric furnace. Silicon nitrides SiN_2 , Si_2N_3 , and Si_3N_4 , are formed when nitrogen is passed over heated silicon. The nitride $\text{N}=\text{Si}=\text{Si}=\text{N}$ is formed by strongly heating the product of interaction of Si_2Cl_6 and ammonia.

Silicon disulphide SiS_2 is formed in white silky needles by heating silicon in sulphur vapour: it is decomposed by water into hydrogen sulphide and gelatinous silica. It is also formed by passing the vapour of carbon disulphide over a strongly heated mixture of silica and carbon: $\text{SiO}_2 + \text{CS}_2 + \text{C} = \text{SiS}_2 + 2\text{CO}$. It forms long fibre-like molecules:

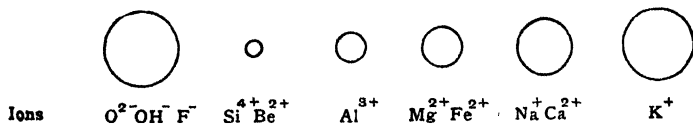


The structure of the silicates.—In the silicates the fundamental unit is the orthosilicate ion SiO_4^{4-} , in which the silicon is tetrahedrally surrounded by four oxygens. The distance $\text{Si}-\text{O}$ is 1.62A. and the distance $\text{O}-\text{O}$ is



2.7A., as determined by X-ray methods. Four electrons are drawn from the oxygens O^{2-} to the silicon Si^{4+} , and the ion has the negative charge uniformly distributed over the four oxygens, the central silicon being neutral. The tetrahedral structure is represented in projection, each oxygen being shown as a circle O , and the silicon by a dot \bullet , the silicon being shown inside the oxygen at the apex. It must be noted that each oxygen is joined to silicon by only one link and is not joined to other oxygens, the sides of the tetrahedron merely indicating the arrangement in space.

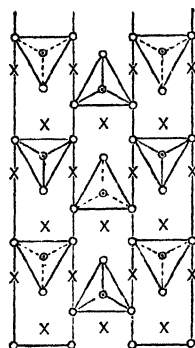
1. In orthosilicates the SiO_4^{4-} ions are independent, and the charges are balanced by the positive charges of cations packed in the lattice in the inter-



stices of the silicate ions. The radii of the metal (and silicon) ions are (except in the case of calcium and alkali metals) small compared with the

radius of the oxygen ion, so that the structure is practically determined by the packing of the oxygens.

In orthosilicates the positive ions are usually bivalent, *e.g.* in olivine Mg_2SiO_4 the SiO_4^{4-} tetrahedra are arranged alternately orientated in parallel rows, with Mg^{2+} ions interposed, as shown. Each Mg^{2+} (shown as \times) is surrounded by 6 oxygens slightly distorted from an octahedral arrangement.



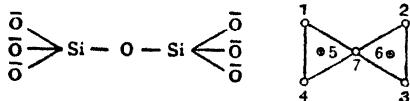
2. In silicates other than orthosilicates **two types of oxygen linkage** are recognised :

(a) The oxygen atom belongs to two silicon atoms, *i.e.* is linked on both sides to silicon, when its valencies are saturated and the linkage is covalent.

(b) The oxygen atom is linked on one side only to silicon, when it has one negative charge which can be neutralised by a positive cation :

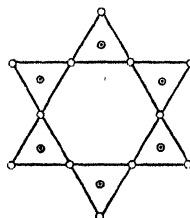
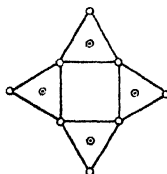
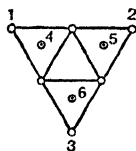


For example, the ion $Si_2O_7^{6-}$ may be represented as two tetrahedra meeting in a corner. The oxygens 1 to 6 (type b) each contribute -1 to the valency, but the oxygen 7 (type a) is linked on both sides and is neutral.



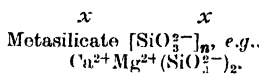
3. Various more complicated silicate ions may be built up from the fundamental SiO_4^{4-} group in the manner shown below. Each arrangement, which contains linkages of types *a* and *b*, forms a self-contained anion, neutralised by positive cations in the lattice. The anions may consist of :

(A) Rings of 3, 4 or 6 silicon atoms with an equal number of oxygen atoms linked on both sides between them. The valency of each group is given by the number of oxygen atoms linked on *one side only* (case *b*) to silicon : *e.g.* numbers 1 to 6 in the first figure :

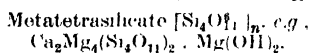
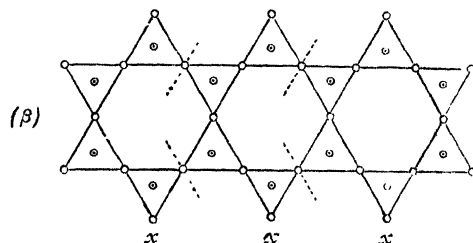


(B) Chains, fibres, or bands, formed by linking pairs of silicon atoms through oxygen and capable of extending indefinitely in length. The valency is again -1 for each oxygen singly linked to silicon (type *b*). Two arrangements may be distinguished.

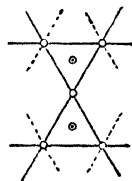
In the first (α) each unit as shown between dotted lines contains one silicon singly linked to two oxygens of type *b*, 1 and 2, giving the valency of -2 , and sharing two half-oxygens 3 and 4 of type *a* (valency zero) with two other silicons; i.e. each silicon is associated with $2 + 2 \times \frac{1}{2} = 3$ atoms of oxygen in all, making up the metasilicate ion, SiO_3^{2-} . The end units, making up only a small fraction of the lattice, are disregarded.



The second arrangement (β) is formed by joining two (α) arrangements through the oxygens marked *x*, thus forming a band from a chain. The unit shown between dotted lines contains 4 silicons associated with $9 + 4 \times \frac{1}{2} = 11$ oxygens in all, and of these 6 are singly linked to silicon (type *b*), giving the valency -6 to the unit.

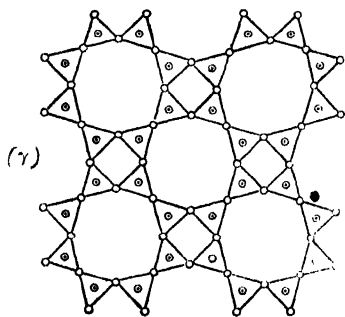


tetrahedron are linked on both sides and have zero valency, one oxygen is singly linked and has the valency -1 . The unit of such an arrangement, shown between dotted lines, is $\text{Si}_2\text{O}_7^{2-}$; two silicon atoms are linked with $3 + 4 \times \frac{1}{2} = 5$ oxygens, and there are 2 singly linked oxygens (type *b*) giving the valency -2 . It is unnecessary to draw the arrangement $[\text{Si}_2\text{O}_7^{2-}]_n$ in full, as it is easily visualised as formed of two β strips. This is the ion of the disilicates, e.g. talc, $\text{Mg}_3(\text{Si}_2\text{O}_7)_2$, $\text{Mg}(\text{OH})_2$. In mica, one in four of the tetrahedral groups of oxygens surrounds Al instead of Si (see below). The arrangement

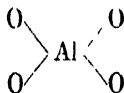


also a disilicate, the unit being again $\text{Si}_2\text{O}_7^{2-}$. Any arrangement of SiO_4 tetrahedra in sheets, linked through oxygens, gives the same unit ion.

(D) If every corner of the SiO_4^{4-} tetrahedron is linked through oxygen we obtain a **three-dimensional lattice**. Every oxygen is shared and there are no free valencies. The structure contains two oxygens to every silicon atom and is electrically neutral: it is silica, the structure of which has been represented in this way on p. 659. If, however, a silicon is replaced by an aluminium ion of charge $+3$ instead of $+4$, tetrahedrally surrounded by four oxygens, the central Al now has a charge -1 , since it is unable to



neutralise the 4 negative oxygen charges drawn to the centre. This extra charge may be balanced in the lattice by additional cations. The arrangement is present in the aluminosilicates: *e.g.* $(\text{NaAl})\text{Si}_3\text{O}_8$ forms $\text{CaAl}_2\text{Si}_2\text{O}_8$ by replacing $\overset{+}{\text{NaSi}}$ by $\overset{++}{\text{CaAl}}\overset{-}{}$:



Replacing some silicon by aluminium gives a large negatively charged lattice, like a vast extended acid radical, which can absorb cations to assume electrical neutrality. Examples are the zeolites, the sponge-like lattice of which remains unaltered when metal ions are exchanged, *e.g.* $(\text{Ca}^{2+} \text{ for } 2\text{Na}^+)$. This explains the ready exchange of such ions in water softeners (p. 185).

CHAPTER XXXV

METALS AND ALLOYS. SPECTRUM ANALYSIS

Metals.—Only a few metals, viz., gold and the platinum metals, usually occur in the metallic or native state; the rest occur as ores, mostly oxides and sulphides, or carbonates and sulphates, although some metals, e.g. copper, silver, and mercury, are also found native. The principal methods used for the extraction of metals may be briefly summarised.

Native copper, gold and the platinum metals are worked up by refining. Other industrial processes for the extraction of metals include (small scale extractions in brackets):

- (1) reduction of the oxides with hydrogen: tungsten; (all metals with atomic weights greater than that of manganese);
- (2) reduction of oxides with carbon: zinc, cadmium, aluminium (electrolytic), tin, bismuth, manganese, iron, cobalt, nickel, lead, copper; titanium, zirconium, thorium in the electric furnace; many special steels by simultaneous reduction of the oxide with carbon and iron; (metals after group III, some at high temperature in the electric furnace);
- (3) reduction of oxides with aluminium (*thermit process*): chromium, manganese, (molybdenum, vanadium, cerium); (on the small scale magnesium, or mischmetall, p. 821, may replace Al);
- (4) oxidation of sulphides, either directly by atmospheric oxygen as with mercury ($\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$), or by partial oxidation and inter-action of sulphide with oxide or sulphate as with copper (p. 719) and lead (p. 834);
- (5) reduction of sulphides with iron: antimony, tungsten, (mercury);
- (6) electrolytic processes: electrolysis of (a) fused hydroxide for sodium (potassium, etc.); (b) fused chloride for magnesium and calcium (beryllium, strontium, etc.), or the oxide dissolved in fused cryolite for aluminium; (c) solutions of salts for copper, silver, gold, zinc, nickel, chromium; (with a mercury cathode for several metals, followed by heating the amalgam);
- (7) special processes; carbonyl process for nickel (p. 946).

Alloys.—Two or more metals when fused together usually (but not always, e.g. zinc and lead, p. 735), form a homogeneous liquid, and the metal formed on solidification is called an *alloy*. Although the preparation of alloys by fusion is the method commonly used, the strong compression of finely-powdered metals, the simultaneous electro-deposition of the metals from a mixed solution (e.g. copper and zinc in the form of brass, from a solution of the cyanides in potassium cyanide), and the reduction of one or more of the metals from compounds in the presence

of the other metal (*e.g.* tungsten and iron compounds in the electric furnace), are alternative processes. Alloys containing mercury are called *amalgams*.

An alloy may be either homogeneous or heterogeneous. The homogeneous alloy may be: (i) a *solid solution*; (ii) a *pure chemical compound*; or (iii) a *solid solution of a compound in excess of one of the metals*.

If the alloy is heterogeneous the separate phases may consist of: (i) *pure metals*, (ii) one or more *pure compounds*; or (iii) *solutions of metals or their compounds, in metals*.

Compounds of metals with non-metals may form alloys: hard steel, prepared by quenching, is a solid solution of iron carbide Fe_3C in a particular allotropic form of iron (γ -iron).

Freezing-point curves of alloys.—The class to which an alloy belongs may be determined by an examination of the freezing points of fused mixtures of the metals. For simplicity consider only two metals.

Consider first the case in which *no chemical compounds are formed* (*e.g.* antimony and lead). If pure antimony is fused and allowed to cool it

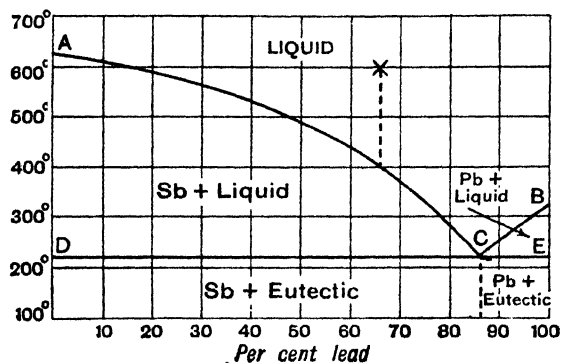


FIG. 348.—Freezing-point curves for antimony and lead.

solidifies completely at the temperature 630° shown at *A* in Fig. 348. If a little lead is added to the fused antimony, the alloy begins to solidify at a temperature a little below the freezing point of pure antimony, since a dissolved substance lowers the freezing point of antimony (provided pure antimony separates on freezing, p. 249). Increasing amounts of lead cause a lowering of freezing point along the curve *AC*. If the molecular depression of freezing point were constant, *AC* would be a straight line, but it is usually a curve, since the laws of dilute solution do not apply strictly.

In the same way, if the freezing point of pure lead is represented by *B* (327°), addition of antimony to fused lead causes a lowering of freezing point represented by *BC*.

If a fused mixture of lead and antimony of the composition corresponding with the point *C* (about 86 per cent of lead) is cooled, lead and antimony separate together in a constant ratio until the whole has solidified at the constant temperature (about 230°) corresponding with *C*. This is a **eutectic point** (p. 249), and is the lowest temperature at which liquid alloy may be present.

At all points above *ACB* the alloy is entirely liquid; at all points below a horizontal line *DCE* drawn through *C* the alloy is entirely solid. At temperatures in the region *ACD* pure solid antimony separates from the freezing liquid alloy, and at temperatures in the region *BCE* pure solid lead separates.

Now consider what happens when a fused alloy represented by the point X (66 per cent lead) is cooled. It remains liquid until the temperature has fallen to such a point that the freezing-point curve AC is reached. This curve corresponds with the separation of solid antimony, and this will crystallise out. The liquid alloy remaining is enriched in lead and its composition falls to the right of 66 per cent of lead. To cause more solid antimony to separate, the temperature must be lowered slightly, and hence further solidification of antimony corresponds with temperatures along the curve until the point C is reached, when lead begins to separate as well and the whole solidifies at the constant temperature of the eutectic point. The constant temperature corresponds with the constant composition of the liquid during solidification, since antimony and lead now separate in the same ratio as they exist in the liquid.

All completely solidified alloys on the left of C consist of crystals of antimony and a eutectic solid mixture of antimony and lead.

By considering a point in the liquid alloy above the line BC , it will be seen that, on cooling, pure lead will separate when the temperature falls to a point on BC . On further solidification, the liquid alloy is enriched in antimony until the eutectic point C is reached, when lead and antimony separate in a constant ratio until all is solid. The solid to the right of C consist of crystals of lead in a eutectic mixture of lead and antimony.

In the second place consider an alloy in which *metallic compounds are formed*, say tin and magnesium, which form Mg_2Sn . The freezing-point curve is shown in Fig. 349.

The compound Mg_2Sn has a definite melting point 783.4° , represented by C . If pure tin is added to the fused compound, or to a mixture of the metals in the correct proportions, the freezing point is lowered. The solid separating along CE_1 is pure Mg_2Sn .

Finally a eutectic point E_1 is reached, at which Mg_2Sn and Sn separate together. If magnesium is added to pure tin, the freezing point is depressed along AE_1 , the solid separating being pure tin until E_1 is reached, when tin and Mg_2Sn separate. The solid alloy obtained on cooling a liquid mixture of composition C will be homogeneous Mg_2Sn . An alloy formed by the complete solidification of a liquid of a composition enclosed within the verticals between C and E_1 will consist of crystals of Mg_2Sn embedded in a matrix of a eutectic mixture of Mg_2Sn and tin.

Similar relations hold for addition of excess of magnesium to Mg_2Sn , or tin to excess of magnesium, when a second eutectic point E_2 will appear. Between E_2 and B pure magnesium separates, between E_2 and C pure Mg_2Sn , at E_2 the eutectic Mg_2Sn with magnesium separates.

If we commence with pure tin and add increasing amounts of magnesium,

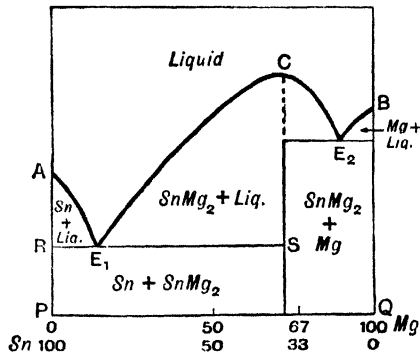


FIG. 349. -Freezing-point curves of binary alloy forming one compound.

the freezing points make up the curve AE_1CE_2B , which has a maximum and two eutectics. A curve of this type is characteristic of the formation of one compound. If there are two compounds there will be two maxima, and so on. The rounded form of the maximum indicates that the compound is partly dissociated in the liquid state: $Mg_2Sn \rightleftharpoons 2Mg + Sn$. The microscopic appearance of a pure metal, or of an alloy which is a definite compound, is that of more or less large crystals which are practically in contact, since there is no eutectic matrix.

The ordinary valency rules cease to apply to alloys (inter-metallic compounds). An empirical rule (Hume-Rothery, 1926) states that the ratio of the number of atoms to the number of valency electrons is the same for structurally analogous compounds: e.g. 13 : 21 for Cu_5Zn_8 , Cu_9Al_4 , $Cu_{31}Sn_8$; 2 : 3 for $CuZn$, Cu_3Al , Ag_3Al , Cu_5Zn ; and 7 : 4 for $CuZn_3$, $AgZn_3$, $AgCd_3$. In compounds of Fe, Co, Ni, Pd, and Rh the valency of these elements must be taken as zero.

SPECTRUM ANALYSIS

White light, when passed through a glass prism is broken up into a series of coloured rays called a spectrum. The rays of different colours are bent or refracted by the prism to different extents; the spectrum shows the colours in the order: red, orange, yellow, green, blue, indigo and violet, the red being least refracted. This is a continuous spectrum without any gaps. At the red end beyond the visible part, are rays which may be detected by their heating effect. These are the *infra-red rays*.

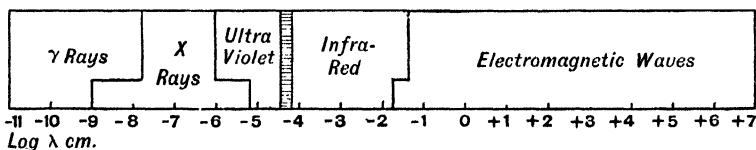


FIG. 350.

Beyond the violet there are also invisible rays, which may be detected by causing the fluorescence of quinine salts and some other substances. These are the *ultra-violet rays*.

Each kind of radiation has a definite *wave-length* λ . The *infra-red waves* are the longest and the *ultra-violet waves* the shortest. Wireless waves are very long; X-rays and γ -rays are very short. Wave-lengths of radiation are usually measured in tenth metres, *i.e.*, 10^{-10} m. or *Ångström units* (A.U.). The μ and $m\mu$ units (p. 4) may also be used.

Fig. 350 gives the wave-lengths (λ) of all parts of the spectrum. The visible spectrum (shaded) extends only over the very restricted range of 4000 to 7000 A.U.

Small quantities of various salts, heated on platinum wire in a Bunsen flame, impart characteristic colours to the flame:

sodium salts: yellow
 potassium salts: lilac
 lithium salts: crimson

thallium salts: green
 strontium chloride: red
 calcium chloride: orange-red.

If the light emitted is passed through a prism, the spectra consist of separate lines, each corresponding with a definite wave-length, *i.e.* they are **line spectra**: the spectrum of every element is characteristic, and can serve for its identification. This is the principle of **spectrum analysis**, introduced by Bunsen and Kirchoff in 1859.

The spectra of salts usually correspond with those of the metals contained in them: that of sodium chloride is identical with the spectrum of metallic sodium. The salt vapours at the high temperature of the flame are dissociated into their elements. In some cases a compound shows a characteristic spectrum; calcium chloride first gives a spectrum of the chloride, and later a spectrum corresponding with calcium oxide.

The **band spectra** of molecules consist of luminous bands, often with a fluted appearance (Fig. 351). A spectroscope of high resolving power shows that the bands consist of large numbers of fine lines.

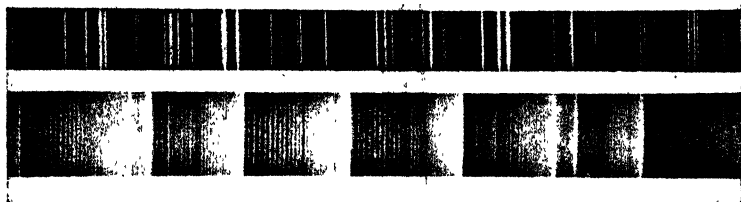


FIG. 351. —Line and band spectra of nitrogen.

(By courtesy of Prof. A. Fowler.)

Line spectra are produced by atoms, band spectra by molecules or radicals (sometimes not known as stable forms, *e.g.* C_2 or PO). A band spectrum consists of relatively widely separated groups of lines, each group due to an electronic energy-change as in the production of line spectra (p. 427). In each electronic group there are lines due to changes of the vibrational energy of the atoms in the molecule, and between pairs of these vibrational lines there are equally spaced lines closer together and due to changes in the rotational energy of the whole molecule. The electronic, vibrational, and rotational energies are quantised, and the structure of band spectra will give information about the interatomic distances and angles in molecules (p. 439).

Electronic spectra occur in the ultra-violet or visible region. Vibrational transitions are usually accompanied by rotational, and the vibration-rotation and rotation spectra (generally observed as absorption bands) occur in the near and far infra-red when present alone, but when they form part of the fine-structure of an electronic band they are found in the corresponding part of the spectrum.

In Raman spectra (p. 439) the frequency-difference between the incident and changed lines is equal to a vibrational frequency of the scattering molecule and is independent of the frequency of the incident light. In this way the molecular vibrational frequency appears in the visible spectrum, and is more easily measured than in an ordinary absorption spectrum in the infra-red region of the spectrum.

The spectroscope.—The spectroscope was invented by Bunsen and Kirchhoff (Fig. 352).

It has a prism *a* of flint-glass, supported on an iron stand, and a brass tube *b*, called a collimator, fitted at the end farthest from the prism with an

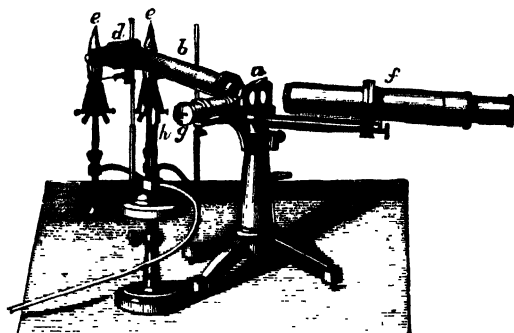


FIG. 352.—Simple spectroscope.

adjustable slit *d*. In this way a narrow line of light from the Bunsen flame *e*, in which the substance is heated, is focused on the prism, the rays being made parallel by a lens in the collimator. The light passing through the prism is received by the telescope *f*, which may be moved round so as to embrace any part of the spectrum, and contains a lens which

gives a magnified view of the spectrum in the eye-piece. In order to fix the position of any particular line, the image of a glass scale fixed in the third tube *g*, and illuminated by a luminous gas flame is thrown by reflexion on the face of the prism into the telescope, and appears above the spectrum. The position of the line is then read off by comparison with this scale.

Production of spectra.—The spectra of gases may be observed in the light emitted by the gas at low pressure (1–2 mm.) when subjected to the electrical discharge from a coil in a Geissler tube. Volatile salts may be heated on platinum wire, moistened with hydrochloric acid, in a Bunsen flame; or a small fused bead of the salt (usually the chloride) heated on the wire. The spectra of liquids may be obtained by taking electric sparks near the surface between platinum wires, as shown in Fig. 353. The spectra of difficultly volatile substances are obtained by heating a small quantity of the material in a little hollow in the lower carbon rod of an electric arc. The spectra of some metals (*e.g.* iron) may be obtained by striking an arc, or passing powerful sparks, between rods of the substance.

The spectroscope can show the presence of very minute quantities of certain elements—far below the possibility of detection by chemical analysis. A quantity of $\frac{1}{3000000}$ mgm. of sodium may be detected, and all ordinary materials show the spectrum of this element. In other cases the spectroscope may be much less sensitive, and sometimes the spectrum of one substance may practically be extinguished by traces of other substances.

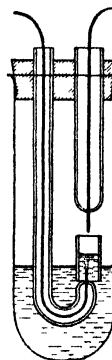


FIG. 353.—Apparatus for producing spark spectra.

The solar spectrum.—In 1802 Wollaston, examining sunlight by means of a prism, noticed that the spectrum was crossed by a large number of fine *black* lines. These dark lines, carefully mapped by Fraunhofer in 1814, are called **Fraunhofer's lines** and the most important are designated by alphabetical letters. Fraunhofer suggested that they were caused by the *absorption* of the particular parts of the spectrum by the passage of the light through the atmosphere of incandescent gases surrounding the sun. Kirchoff in 1860 repeated an experiment made by Foucault in 1848. He brought near the slit of the spectroscope, through which he was examining the solar spectrum, a flame charged with sodium vapour. The two very nearly coincident dark lines in the solar spectrum, called D by Fraunhofer, at once changed into the two bright yellow lines of the sodium spectrum, which were therefore coincident with the dark D-lines of the solar spectrum. Kirchoff then exchanged the sunlight for limelight, which gives a continuous spectrum having no dark lines. On placing a sodium flame between the source of this light and the slit of the spectroscope, the two dark D-lines at once appeared.

Kirchoff pointed out that this result is easily explained by supposing that the sodium flame absorbs the same kind of rays as it emits, whilst it is transparent to other rays. If the intensity of the light passing through the flame is greater than that of the light emitted by the flame, the absorption will cause such a weakening of intensity in that part of the spectrum that the lines will appear dark in contrast with the rest of the spectrum.

Pass a stream of hydrogen through a Woulfe's bottle in which hydrogen is produced from zinc and dilute hydrochloric acid containing common salt. The gas is burnt as a large flame, coloured yellow by sodium from the spray, at a burner (Fig. 354). A small Bunsen burner with a bead of sodium chloride is placed in front of the large flame. The outer edge of the small flame appears dark against the bright yellow background.

The presence of sodium vapour in the atmosphere of the sun may be inferred from the *dark* lines in the spectrum. The *bright* parts of the spectrum teach us nothing, because they are merely parts of the continuous spectrum emitted by *any* body raised to incandescence. The *dark* lines of the spectrum, corresponding with absorption in the solar atmosphere, indicate the presence of corresponding elements in the sun. Certain stars and nebulae show *bright* lines on a dark ground. These correspond with elements present in the masses of incandescent gas or vapour.

The spectroscope opened the way to the chemical examination of bodies in space; the rays of light coming from the most distant stars

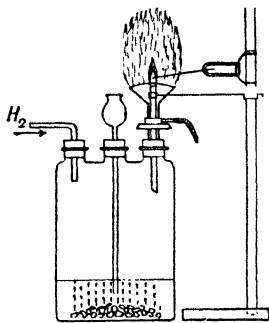


FIG. 354. - Reversal of sodium line.

reveal the chemical composition of the luminous matter with as much certainty as if the millions of miles of intervening space had been annihilated, and a sample of the star placed on the laboratory bench.

Absorption spectra.—If white light passes through a transparent coloured body, such as ruby glass or a solution of indigo, the emergent light when examined by the spectroscope is found to have lost certain

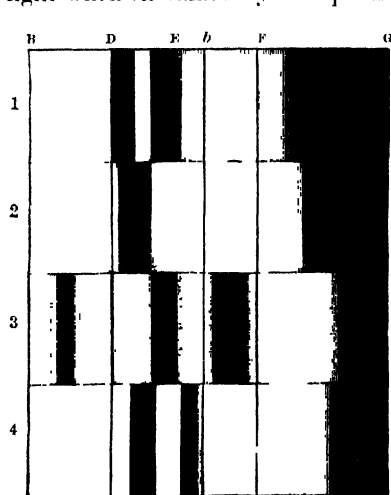


FIG. 355.—Absorption spectra of blood.

The absorption spectra of salt solutions are nearly always made up of one or two sets of bands, corresponding with one or both of the two ions. All permanganates show the same bands, characteristic of the ion MnO_4^- . The absorption spectra of blood are shown in Fig. 355. No. 1 shows two dark bands, D and E, due to oxyhaemoglobin, given by oxidised blood. No. 2 shows the absorption spectrum of de-oxidised blood, in which there is only one dark band, due to haemoglobin. By the action of acids on blood, the haemoglobin is converted into haematin, the oxidised and de-oxidised forms of which give the spectra Nos. 3 and 4. Carbon monoxide, nitric oxide and hydrocyanic acid form compounds with haemoglobin giving characteristic absorption spectra, and this is used in detecting carbon monoxide in cases of poisoning by that gas.

An important application of absorption band spectra is in the determination of heats of dissociation. Consider a gas composed of diatomic molecules A_2 and suppose it to be traversed by radiation of frequency ν which is absorbed. (This will usually be in the ultra-violet.) The molecule absorbs a quantum $h\nu$ which brings about a vibration of the two atoms. The absorption is marked by a vibrational line in the absorption spectrum, and this usually has a fine-structure due to rotation (p. 677). As ν increases a succession of vibrational-rotational levels is traversed, the lines drawing closer and closer together because the vibration is not a simple harmonic motion, and departs from this all the more as the amplitude increases. When the amplitude of vibration carries the two atoms beyond the range their attractive forces, they separate and the molecule dissociates: $\text{A}_2 = 2\text{A}$. The energy then ceases to be quantised vibrational energy, and the spectrum beyond this limiting frequency ν_d is continuous. The energy

required to dissociate the molecule is $h\nu_d$ (or $Nh\nu_d$, where N is Avogadro's number, per mol.) This may require correction if one or both of the atoms A formed is excited, *i.e.* has more energy than in the normal state.

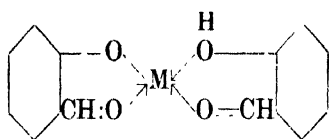
CHAPTER XXXVI

THE ALKALI METALS

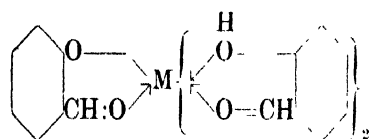
GROUP I of the Periodic Table contains two groups of metals, (i) the *even series* or sub-group *a*, of the **alkali metals**, and (ii) the *odd series* or sub-group *b*, comprising **copper, silver and gold**. The odd and even series show startling differences, and would never have been brought into the same group on purely chemical grounds.

The alkali metals are the most strongly electropositive elements known, the positive character increasing with atomic weight from lithium to caesium. The elements of the odd series have a much less pronounced electropositive character and this decreases with rise of atomic weight, gold being one of the most weakly electropositive metals. The alkali metals oxidise with the greatest ease and decompose water violently; copper oxidises in air only appreciably on heating and decomposes water only at a very high temperature, whilst silver and gold are "noble" metals, which can be heated to redness in air without oxidation. Lithium shows marked differences from the other alkali metals and in many ways resembles magnesium, its neighbouring element in Group II.

The alkali metals are all univalent in simple compounds and salts, but show valencies of 4 and 6 in some compounds with organic substances, such as salicylaldehyde :



$M = \text{Li, Na, K, Rb, Cs.}$



$M = \text{K, Rb, Cs.}$

Copper shows ordinary valencies of 1 and 2, and sometimes 3; silver valencies of 1 and sometimes 2 and 3, and gold valencies of 1 and 3 of more nearly equal stability. The alkali metals show no tendency to form complex compounds, but this is very marked with copper, silver and gold, which form both cation, *e.g.* $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, and anion, *e.g.* $\text{K}[\text{Ag}(\text{CN})_2]$, complexes and these elements also show a marked tendency to form covalent compounds even with the strongly electronegative halogens, which tend to remove electrons from metal atoms to form positive ions. Cuprous halides have non-ionic (zinc blende) lattices, and fused cuprous chloride is not a good conductor (although fused silver chloride is), and in the vapour state the molecule is Cu_2Cl_2 .

The alkali metal vapours are largely monatomic, but sodium vapour (mol. wt. 24–26) contains some Na_2 molecules (Rodebush and Walters, 1930). In solution in tin, sodium is monatomic. The metals all crystallise in body-centred cubic lattices. They form salt-like hydrides MH and halides MX . The basic oxides are M_2O , but the higher oxides, Li_2O_2 , and M_2O_2 , M_2O_3 , and MO_2 with Na, K, Rb and Cs, are known. The metals are very reactive and combine directly with halogens and sulphur, and lithium with nitrogen. Lithium reacts rapidly with water and sodium violently, but the hydrogen liberated does not inflame; potassium, rubidium and caesium react with increasing violence and the hydrogen inflames.

The alkali metals are reduced from their compounds only with difficulty; the hydroxides are reduced by carbon at high temperatures but most easily by electrolysis.

Since the ammonium compounds, containing the positive univalent ammonium radical NH_4 , show very close resemblances to compounds of the alkali metals they are usually studied along with the latter.

The properties of the alkali-metals are shown in the table below.

	Lithium.	Sodium.	Potassium.	Rubidium.	Caesium.
Atomic number	3	11	19	37	55
Electron configuration	2.1	2.8.1	2.8.8.1	2.8.18 8.1	2.8.18 18.8.1
Density at 0°	0.5	0.9723	0.859	1.525	1.903
Atomic volume	12.9	23.7	45.5	56.1	69.8
Melting point	180°	97.9°	62.04°	39.0°	28.45°
Boiling point	1336°	882.9°	762°	700°	670°
Colour of vapour	?	purple, yellow fluorescence	green	greenish-blue	blue
Action on water	slow	rapid, hydrogen does not burn	rapid, hydrogen burns	rapid; hydrogen burns	rapid; hydrogen burns
Oxides	Li_2O Li_2O_2	Na_2O Na_2O_2 Na_2O_3 NaO_2	K_2O K_2O_2 K_2O_3 KO_2	Rb_2O Rb_2O_2 Rb_2O_3 RbO_2	Cs_2O Cs_2O_2 Cs_2O_3 CsO_2

The salts of the alkali metals are colourless unless the acid ion (*e.g.* in chromates and permanganates) is coloured. The alkali polysulphides are yellow or red.

SODIUM

History.—Metallic sodium and potassium were discovered by Davy in 1807; the method (electrolysis of fused caustic alkali) was first tried with potash, and potassium was the first alkali metal isolated. Davy says:

“A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface [by attraction of moisture, and slight deliquescence], was placed upon an insulated disc of platina, connected with the negative side of the battery

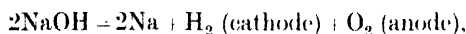
... in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. . . . The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered with a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash."

The experiment may be carried out by laying a piece of moist stick potash on a piece of platinum foil connected with the negative pole of a battery, and touching the potash with a platinum wire connected with the positive pole.

Gay-Lussac and Thenard in 1808 showed that when molten caustic potash or soda is brought in contact with red-hot iron turnings, the iron is oxidised and the alkali metal distils off. At the same time a considerable amount of hydrogen is evolved. The caustic alkalis were then recognised as hydroxides, KOH and NaOH, of the metals potassium and sodium, not the oxides as Davy supposed.

The presence of hydrogen in caustic potash or soda may be shown by heating a mixture of the powdered alkali with iron filings in a hard-glass tube. Hydrogen is evolved, and may be ignited at a jet fixed to the tube.

Metallic sodium.—Sodium may be obtained by heating sodium peroxide with carbon, or sodium hydroxide with magnesium. Although first prepared by Davy from sodium hydroxide by electrolysis:



metallic sodium was for many years produced on the large scale by a process due to Castner (1886): sodium hydroxide was heated with

carbon and iron at 1000° : $6\text{NaOH} + 2\text{C} = 2\text{Na} + 3\text{H}_2 + 2\text{Na}_2\text{CO}_3$. In 1890 Castner, on account of the development of cheap electricity, was able to revert to Davy's original process and sodium is now produced by this method.

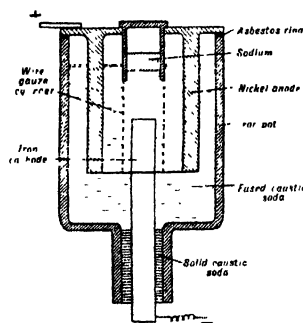


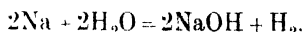
FIG. 356.—Production of sodium by electrolysis.

the cathode. The metal rises from the cathode and floats on the surface of the sodium hydroxide inside a small metal receptacle provided with

a lid. It is removed by a wire-gauze spoon, which allows the fused sodium hydroxide to flow away but retains the sodium. The sodium is sent out sealed up in tin cans in the form of thick rods.

The electrolysis of sodium chloride, alone or mixed with potassium or calcium chloride or sodium fluoride, is also used to some extent in the *Downs cell*, which is similar to the Castner cell except that the central electrode is an anode of carbon from which chlorine is evolved; it is surrounded by an annular iron cathode on which the sodium deposits.

Sodium is a silver-white, very soft metal of low melting point. It may be obtained in octahedral crystals on slow cooling of fused sodium. It is lighter than water. It is a good conductor of electricity (about a third as good as silver). Sodium forms a purple vapour and a purple colloidal solution in ether. Sodium is used in some types of electric discharge lamps. The clean, freshly-cut surface of the metal rapidly tarnishes in the air, so that the metal is usually kept under petroleum. It burns when heated in moist oxygen or chlorine, and acts violently on water :



When a small piece of sodium is thrown on water it moves about rapidly, hydrogen being evolved. The rise in temperature is not sufficient to kindle the hydrogen unless the piece of metal is kept in one place by putting it on starch jelly, when the hydrogen burns with a flame coloured yellow by sodium vapour. (Explosions sometimes result). *Sodium amalgam* is obtained by pressing small pieces of the metal into mercury in a mortar by means of a pestle: each piece reacts with a small explosion and a flash of light. The amalgam is solid if more than 1 part of sodium is added to 80 of mercury.

Sodium hydride. Sodium hydride NaH is prepared by passing a slow stream of dry hydrogen over sodium in a nickel boat heated in a glass tube at 365°. Colourless matted crystals form on the upper cooler portion of the tube just beyond the boat. It is decomposed by water with evolution of hydrogen: $\text{NaH} + \text{H}_2\text{O} = \text{NaOH} + \text{H}_2$, and by concentrated sulphuric acid, with formation of sulphur and hydrogen sulphide. On heating above 330° it dissociates rapidly: $2\text{NaH} = 2\text{Na} + \text{H}_2$. It absorbs carbon dioxide, producing sodium formate: $\text{NaH} + \text{CO}_2 = \text{HCOONa}$.

Sodium chloride. Sodium chloride NaCl, common salt, occurs in nature in cubic crystals of *rock salt*, colourless when pure but often tinged yellow, brown, or sometimes blue, by impurities. Rock salt also occurs in large masses which readily break into small cubes. The richest English deposits are in Cheshire; salt is also found in most other parts of the world. More or less concentrated (about 25 per cent) solutions (*brines*) also occur in many places, or are artificially produced by letting

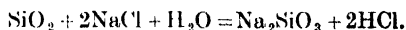
water down to the rock salt and then pumping. The waters of the Dead Sea and the Great Salt Lake of Utah are concentrated solutions of common salt. The Dead Sea water is also rich in bromides, and is now an important source of bromine : it is evaporated, when much common salt separates out, and the residual liquor is then worked for bromine by chlorination (p. 317). Some salt is made in hot climates from sea water (2.5-3 per cent NaCl), which is allowed to evaporate in large flat ponds called " salt meadows " by the heat of the sun, such salt being called " solar salt ". The mother liquor is called *bittern* and contains magnesium bromide.

Usually the brine is evaporated in large flat iron pans over fire flues. The more slowly the evaporation proceeds the larger are the crystals of salt formed : the grades are fine (or table) salt, manufacturer's salt, fishery salt, and bay salt (usually in the form of floating " hoppers ", or cubes with hollow faces). In modern works the brine is evaporated in multiple-effect vacuum pans with steam heat, the calcium and magnesium salts having first been separated by adding lime and then sodium carbonate.

Pure sodium chloride is made in the laboratory by precipitating a saturated solution of common salt with hydrogen chloride gas. It forms a saturated solution in water at 15° containing 35.8 parts of salt to 100 of water (26 per cent) and the solubility increases only very slowly with rise of temperature. By cooling a saturated solution to -10°, or by cooling a hot saturated solution in hydrochloric acid, a hydrate $\text{NaCl}\cdot 2\text{H}_2\text{O}$, is deposited.

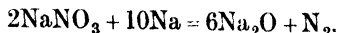
Common salt is used in flavouring and preserving food, preserving hides, as an industrial source of soda, hydrochloric acid and chlorine, in " salting out " soap, melting snow on roads, and glazing common stoneware.

In " salt glazing " stoneware (*e.g.* drain-pipes) common salt is thrown into the furnace in which the goods are fired and is volatilised. In presence of water vapour and the silica of the clay, the salt forms a fusible silicate glaze and hydrochloric acid is evolved :

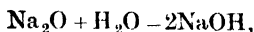


Sodium bromide NaBr and sodium iodide NaI, are similar to the chloride in general properties and are prepared as explained on pp. 322 and 331, respectively. From hot solutions they form anhydrous cubic crystals, but by evaporating at room temperature, monoclinic crystals containing $2\text{H}_2\text{O}$, isomorphous with the corresponding sodium chloride hydrate, are deposited. Sodium fluoride NaF is made by neutralising hydrofluoric acid with sodium hydroxide and forms anhydrous cubic crystals rather sparingly soluble in water. Sodium hydrogen fluoride NaHF_2 or $\text{NaF}\cdot\text{HF}$ is prepared by the reaction $\text{NaF} + \text{HF} = \text{NaHF}_2$.

Sodium oxides.—The two common oxides of sodium are the monoxide Na_2O , and the peroxide Na_2O_2 . Sodium monoxide is obtained either by burning sodium at 180° in a limited supply of air or oxygen and distilling off the excess of metal in a vacuum, or by heating sodium peroxide, nitrate, or nitrite with sodium :

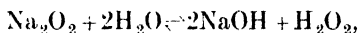


It is a white amorphous mass which decomposes at 400° into the peroxide and metal. It reacts violently with water :

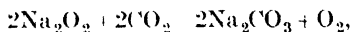


but does not absorb carbon dioxide at the ordinary temperature.

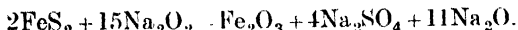
Sodium peroxide Na_2O_2 is obtained by burning sodium in excess of air or oxygen. It is manufactured by heating sodium at 300° in aluminium trays in a current of purified air in iron pipes. In another process the sodium is burnt to monoxide in a revolving iron drum and the monoxide then transferred to a second heat-lagged revolving iron drum where it is oxidised by air to the peroxide. Sodium peroxide is yellow, becoming white on exposure to air from formation of sodium hydroxide and carbonate. When very strongly heated it evolves oxygen. A solution may be prepared by adding the powder in small quantities at a time to a well-stirred mixture of ice and water, a crystalline hydrate $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ being formed. The liquid is strongly alkaline, owing to hydrolysis :



and on warming oxygen is evolved from the hydrogen peroxide. Carbon dioxide decomposes sodium peroxide with evolution of oxygen :



hence the solid has been used for purifying air in confined spaces (*e.g.* in submarines). Carbon monoxide is absorbed: $\text{Na}_2\text{O}_2 + \text{CO} = \text{Na}_2\text{CO}_3$. The solution is an oxidising agent, *e.g.* it converts moist chromic hydroxide into sodium chromate; fused sodium peroxide has powerful oxidising properties, converting chrome-ironstone FeCr_2O_4 into ferric oxide and soluble sodium chromate (p. 889). It also oxidises iron pyrites :



If a little sodium peroxide mixed with sawdust is placed on filter-paper and moistened with water, the mass inflames. Glacial acetic acid inflames when the peroxide is dropped into it. If sodium peroxide is mixed with pieces of recently ignited charcoal and heated in a covered porcelain

crucible, a violent reaction occurs and metallic sodium condenses on the lid of the crucible: $3\text{Na}_2\text{O}_2 + 2\text{C} \rightarrow 2\text{Na}_2\text{CO}_3 + 2\text{Na}$.

When sodium peroxide is treated with absolute alcohol at 0° , a white powder of **sodium hydrogen peroxide** $\text{Na}\cdot\text{O}\cdot\text{O}\cdot\text{H}$, is formed: $\text{Na}_2\text{O}_2 + \text{EtOH} = \text{NaOEt} + \text{NaO}\cdot\text{OH}$. It explodes on heating, evolving oxygen and forming sodium hydroxide. A stable compound, $2\text{NaHO}_2\cdot\text{H}_2\text{O}_2$, is formed on mixing 30 per cent hydrogen peroxide with sodium ethoxide (NaOEt) and absolute alcohol, or by the action of an ether solution of H_2O_2 on sodium. Potassium peroxide forms $2\text{KHO}_2\cdot\text{H}_2\text{O}_2$.

Sodium peroxide is used for making "perborate" (p. 658) and also benzoyl peroxide for bleaching flour.

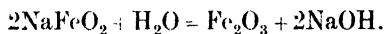
Sodium hydroxide.—Sodium hydroxide or *caustic soda* is obtained very pure by dropping small bits of sodium, or sodium wire from a sodium press, into previously boiled and cooled distilled water in a silver dish, evaporating the solution and fusing the caustic soda (m. pt. 318°). Sodium hydroxide is made on the large scale:

(1) By the electrolysis of a solution of common salt. In the Castner-Kellner cell (p. 205) pure sodium hydroxide is obtained by way of sodium amalgam: in cells in which the brine is not mechanically separated from the sodium hydroxide produced (*e.g.* the Gibbs cell, p. 205), the solution also contains undecomposed common salt, say 12 per cent of each. It is then evaporated in a vacuum evaporator with an arrangement for removing the common salt which separates. When it contains 50 per cent of NaOH , only 1 per cent of NaCl remains. The solution is then evaporated in iron pots over a free fire and the sodium hydroxide finally fused.

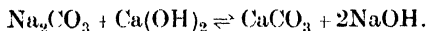
(2) In the **Löwig process**, a mixture of sodium carbonate (soda-ash) and ferric oxide is heated to bright redness in a revolving furnace, when **sodium ferrite** NaFeO_2 (or $\text{Na}_2\text{O}\cdot\text{Fe}_2\text{O}_3$) is formed:



The mass is cooled, broken up, and thrown into hot water, when the sodium ferrite hydrolyses with formation of sodium hydroxide and insoluble ferric oxide, which is used again:



(3) By heating a 20 per cent solution of sodium carbonate with slaked lime in an iron vessel fitted with agitators:



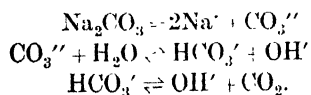
The reaction is reversible, but by using an excess of lime and a solution of sodium carbonate which is not too concentrated, a fairly pure solution is obtained. The filtered solution is evaporated as before, and the sodium hydroxide fused. The commercial sodium hydroxide is supplied fused in drums, or in the form of sticks, coarse powder, or pellets; the last is a convenient form for laboratory use.

Sodium hydroxide is a white slightly translucent solid with a fibrous crystalline texture, m. pt. 318.4°, dissociating at about 1300°: $2\text{NaOH} = 2\text{Na} + \text{H}_2 + \text{O}_2$. Sodium hydroxide is a powerful caustic, breaking down the proteins of the skin and flesh to a pasty mass. When exposed to air it first deliquesces from absorption of moisture and a little carbon dioxide, forming a saturated solution. The solution then slowly resolidifies from absorption of carbon dioxide, when the carbonate Na_2CO_3 , which is sparingly soluble in sodium hydroxide solution, is formed. Potassium hydroxide does not resolidify, since potassium carbonate is readily soluble, and for this reason a concentrated solution of potassium hydroxide is used in gas analysis to absorb carbon dioxide, since it does not deposit solid which would choke the apparatus. There are several hydrates of sodium hydroxide e.g. $\text{NaOH}, \text{H}_2\text{O}$ m. pt. 64°, and $\text{NaOH}, 2\text{H}_2\text{O}$, m. pt. 12.7°.

The densities D_4^{15} of sodium and potassium hydroxide solutions are given in the table :

Per cent.	Density.	
	NaOH.	KOH.
5	1.0555	1.0452
10	1.1111	1.0918
15	1.1665	1.1396
20	1.2219	1.1884
25	1.2770	1.2384
30	1.3310	1.2905
35	1.3835	1.3440
40	1.434	1.399
45	1.482	1.456
50	1.530	1.514

Sodium carbonate.—Anhydrous sodium carbonate (*soda-ash*) is a white amorphous powder, m. pt. 852°, which aggregates on exposure to moist air owing to the formation of hydrates. When added to water much heat is evolved, and the hydrated salt formed usually sets to a mass, which then slowly dissolves. The solution is distinctly alkaline owing to hydrolysis (the decinormal solution is about 3 per cent hydrolysed), and on boiling it slowly loses carbon dioxide :



On evaporating the solution and cooling, large monoclinic crystals of *washing soda* $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$ are deposited. These effloresce in air and on heating at 35.4°, forming a white powder of the monohydrate $\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$, also deposited from hot solutions and known as *crystal carbonate*. Other hydrates are known, e.g. two forms of $\text{Na}_2\text{CO}_3, 7\text{H}_2\text{O}$.

Solutions containing less than 6.3 gm. Na_2CO_3 per 100 gm. water deposit ice on cooling (curve AB , Fig. 357). B is the eutectic point at -2.1° , where ice, solid $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and a solution containing 6.3 gm. Na_2CO_3 per 100 gm. water, are in equilibrium with water vapour. More concentrated solutions do not exist in stable equilibrium with ice and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, yet a solution of 18.46 gm. Na_2CO_3 in 100 gm. water may on cooling become unsaturated with respect to decahydrate and deposits ice at -7.5° . BC is

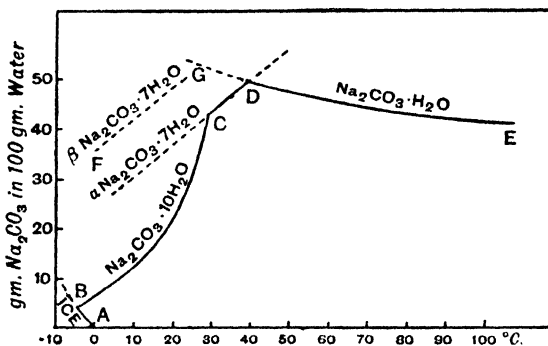


FIG. 357.—Solubility curves of sodium carbonate.

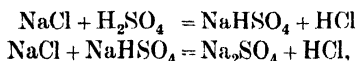
the stable part of the solubility curve of decahydrate (the ordinary "solubility curve"). At C the solid decahydrate changes at 32° into a rhombic heptahydrate, $\alpha\text{-Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$. CD is the stable solubility curve of this hydrate, which may be prolonged on both sides into metastable regions shown by dotted lines. At D the heptahydrate changes at 35.4° into monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the solubility curve of which, with a prolongation into a metastable region shown dotted, is DE . Another heptahydrate, $\beta\text{-Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, which is always metastable, separates along FG .

A compound of sodium carbonate with sodium bicarbonate is **sodium sequicarbonate** $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, which occurs native as *trona* or *urao* in various localities and is produced by the spontaneous evaporation of soda lakes, e.g. in Egypt. Large deposits occur in Owens Lake in California, and Lake Magadi in British East Africa. The sesquicarbonate is also made artificially by crystallising equimolecular amounts of carbonate and bicarbonate from a solution in warm water; the artificial salt is known as *concentrated soda crystals* and is used in wool washing. It is neither efflorescent nor deliquescent.

Sodium carbonate is manufactured from common salt by the Leblanc process (now almost obsolete) and the Ammonia-Soda process. Sodium carbonate was formerly prepared by burning plants growing on the seashore (*Chenopodium*, *Salicornia*, *Salsola* etc.), the ash being called *barilla* and used in the manufacture of soap. When Stahl pointed out that the base of common salt is an alkali, attempts were made to obtain soda from this source. An early process was that of Scheele (1773), in which salt is decomposed by boiling with litharge: $2\text{NaCl} + 4\text{PbO} + \text{H}_2\text{O} = 2\text{NaOH} + \text{PbCl}_2 + 3\text{PbO}$. The same chemist also observed that a

mixture of lime and salt when moistened, slowly effloresced in air with the formation of sodium carbonate. The first satisfactory preparation of alkali from common salt was the Leblanc process (1787).

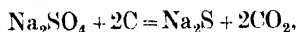
The Leblanc process.—In this process, sulphuric acid is heated with common salt to form sodium sulphate (*salt-cake*) as described on p. 210 :



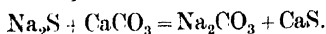
the hydrochloric acid being absorbed in water.

The sulphuric acid may be made from pyrites, in which case the burnt pyrites may contain copper and sometimes silver and gold, which are extracted as a part of the process.

The salt-cake is then mixed with carbon (coal slack) and crushed limestone and heated in a *black-ash furnace* (Fig. 358), which is a large revolving iron cylinder lined with firebricks, through which flames from a gas producer pass. The sodium sulphate is reduced to sodium sulphide by the carbon :



and the sodium sulphide then reacts with limestone to form sodium carbonate and calcium sulphide :



When reaction is complete the red-hot pasty mass is discharged through a man-hole and when cool is lixiviated with water in tanks to dissolve the sodium carbonate, leaving the calcium sulphide and impurities as *alkali waste*. The solution may be evaporated in pans to make crude sodium carbonate, but is usually heated with slaked lime to form sodium hydroxide. Since the product is impure and may contain sodium sulphide, some sodium nitrate is added to the fused sodium hydroxide to oxidise the sulphide, when a white product is obtained, but this contains sodium nitrite and sulphate as impurities.

The complete Leblanc process is dying out, but sodium sulphate (*salt cake*) is made for the sulphate process for making cellulose from wood pulp.

The ammonia-soda process.—When carbon dioxide is passed into a nearly saturated solution of common salt containing ammonia,

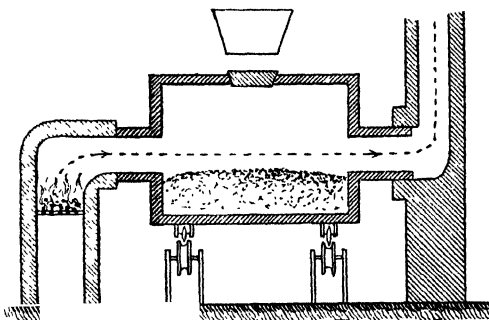
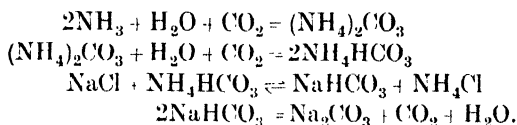


FIG. 358.—Black-ash revolving furnace.

ammonium carbonate is formed and this tends to pass into ammonium bicarbonate, which reacts with the sodium chloride to form sodium bicarbonate and ammonium chloride. Sodium bicarbonate is sparingly soluble in a solution of sodium chloride or ammonium chloride, and mostly separates as a solid which may be filtered off and heated to form sodium carbonate :



The reaction was discovered by Fresnel about 1810. It was worked for a year or two in Scotland by John Thom in 1836 but was not successful. Dyar and Hemming took out a patent for it in 1838 and worked it for a short time in London. It was also worked near Paris by Schloesing and Rolland in 1855, but was first successfully used by Ernest Solvay, whose first patent was taken out in 1861, but whose process was first worked on a large scale near Nancy in 1872. The Solvay process was introduced into England in 1874 by Ludwig Mond and John Brunner, whose works at Northwich in Cheshire is still operated by Imperial Chemical Industries Ltd.

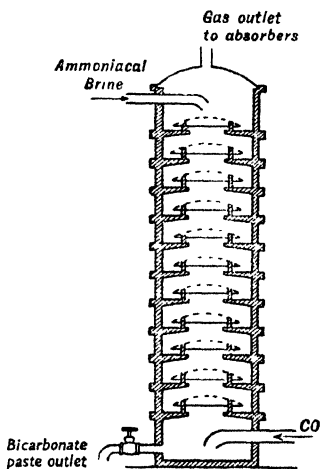
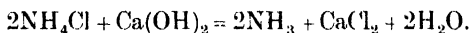


FIG. 359.—Carbonating tower.

In the ammonia-soda process salt brine nearly saturated with common salt is taken and ammonia gas dissolved in it in an iron tower fitted with bubblers. Carbon dioxide is then bubbled under pressure into the ammoniacal brine in a second iron *carbonating tower* (Fig. 359) fitted inside with perforated bubblers, the lower part of the tower being cooled by iron pipes (not shown in the figure) through which cold water circulates. The sodium bicarbonate precipitates and the liquid containing it in suspension is passed to rotating suction filters, on which the solid sodium bicarbonate is washed with a little

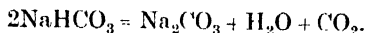
water. The mother liquor contains the undecomposed common salt and ammonium carbonate and chloride; it is passed to ammonia stills where it is heated by steam with milk of lime to recover the ammonia :



The reaction $\text{NaCl} + \text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ is reversible and only about two-thirds of the common salt is converted into bicarbonate the rest is wasted together with the chlorine of the decomposed salt, which forms calcium chloride in the ammonia stills.

The sodium bicarbonate from the filters is calcined in closed tubular

calcining pans, fitted with scrapers which push the solid along the pan. Carbon dioxide is evolved :

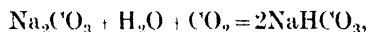


This nearly pure carbon dioxide ("roaster CO_2 ") is mixed with the scrubbed gas containing carbon dioxide and nitrogen from *limekilns*, where the limestone is burnt mixed with coke to produce lime for the ammonia stills. The mixed gas is passed to the carbonating towers.

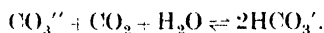
Sodium carbonate or *soda-ash* issues from the calcining pan. This is nearly pure (99.5 per cent) and usually contains only a little sodium chloride from the mother liquor left in the bicarbonate on the filters.

From the *soda-ash washing soda* $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ is made by dissolving in hot water and crystallising. *Crystal carbonate* $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is formed by evaporation and separates from the hot solution. *Concentrated soda crystals* $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ are made by crystallising a hot solution of equimolecular amounts of carbonate and bicarbonate. Sodium hydroxide is made by boiling a solution of the carbonate with lime, as described on p. 688. The ammonia-soda process is more economical and gives a purer product than the Leblanc process.

Sodium bicarbonate.—Sodium hydrogen carbonate or sodium bicarbonate is formed in large quantities in the ammonia-soda process, but is all converted into carbonate, the bicarbonate of commerce being prepared from the latter. A concentrated solution or moist crystals of sodium carbonate when saturated with carbon dioxide give a white crystalline powder of bicarbonate. This may be washed with a little cold water, in which it is sparingly soluble, and dried in the air :

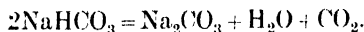


or

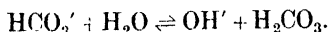


The precipitation is due to the fact that in concentrated solutions the solubility-product $[\text{Na}'] \times [\text{HCO}_3']$ of the salt is exceeded.

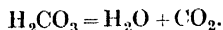
The precipitated bicarbonate is freed by washing from impurities contained in the original carbonate (*e.g.* NaCl), since these are more soluble, and if it is gently ignited in a platinum crucible pure sodium carbonate is formed, which may be used as a standard in volumetric analysis :



The solution of the bicarbonate is slightly hydrolysed and has an alkaline reaction, although much feebler than that of the carbonate :



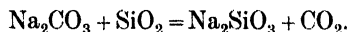
On heating the solution, carbon dioxide is evolved :



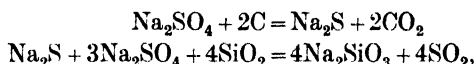
By prolonged boiling practically all the bicarbonate is converted into carbonate, and if crude bicarbonate from the ammonia-soda process is boiled with water the ammonium salts present in it as impurity are decomposed and ammonia is evolved. On recarbonating, by passing

in carbon dioxide, nearly pure sodium bicarbonate is precipitated, and the commercial salt is made in this way.

Sodium silicate.—Sodium silicate (*soluble glass*) is made by melting together sodium carbonate and powdered quartz or pure sand in a reverberatory furnace at a high temperature. Various silicates are formed, and the composition may vary from $\frac{2}{3}$ to 4 SiO₂ to 1 Na₂O :



A mixture of sodium sulphate (*salt-cake*) and powdered coal may be substituted for sodium carbonate :



but sodium carbonate is now mostly used. The product is a greenish-blue glass (brown if sodium sulphide is present), which when broken up and heated with water under pressure in autoclaves slowly dissolves to a thick solution called *water glass*, which may contain 2 to 4 molecules of SiO₂ to 1 molecule of Na₂O. It is alkaline and is used in adding to soap, impregnating wood, weighting silk, as a mordant, in making bricks non-porous, as an adhesive in making cardboard boxes, treating cement floors to reduce dust and abrasion, for preserving eggs, and other purposes. The crystalline sodium metasilicate Na₂SiO₃·5H₂O is readily soluble in cold water and is used in laundries.

Sodium nitrate.—Sodium nitrate NaNO₃ can be prepared in the usual way from nitric acid and sodium hydroxide or carbonate, but occurs native in large deposits in the rainless districts of Chile, hence it is often called "Chili saltpetre" or "Chili nitre".

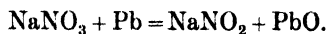
The sodium nitrate in the deposits constitutes from 20 to 50 per cent in a distinct stratum of earth known as *caliche*. The caliche is crushed and lixiviated in large tanks of water heated by steam. The settled solution is run off to crystallisers, where crude nitrate separates, the mother liquors being run back to the lixiviators. The crystals are washed with a little water and dried in the sun : they contain 95-96 per cent of NaNO₃. Most of the export of Chile nitre is used directly as a fertiliser ; the remainder is used to make potassium nitrate and nitric acid.

Sodium nitrate crystallises in rhombohedra resembling cubes, isomorphous with calcite, hence it is sometimes called "cubic nitre". It differs from potassium nitrate in being deliquescent. It melts at 316° and at higher temperatures evolves oxygen, leaving sodium nitrite :

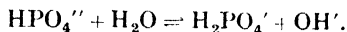


The reduction occurs at a lower temperature in presence of lead, which is oxidised.

Sodium nitrite NaNO₂ is made by heating sodium nitrate with lead (p. 551) :

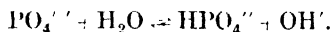


Sodium phosphates.—Ordinary (secondary) sodium phosphate (*disodium hydrogen phosphate*) is prepared by neutralising phosphoric acid with sodium hydroxide or carbonate and evaporating. It forms efflorescent monoclinic crystals $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, readily soluble in water. The effloresced salt contains $7\text{H}_2\text{O}$. The solution is faintly alkaline :



Microcosmic salt or sodium ammonium hydrogen phosphate $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, is formed by dissolving 6 gm. of ammonium chloride and 36 gm. of ordinary sodium phosphate in a little hot water, filtering from the sodium chloride, and crystallising.

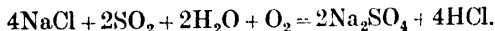
The primary sodium phosphate $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (*sodium dihydrogen phosphate*) is prepared by adding phosphoric acid to a solution of the ordinary phosphate until a little of the solution no longer precipitates barium chloride, evaporating and crystallising. **Trisodium phosphate** is prepared by dissolving ordinary sodium phosphate and sodium hydroxide in hot water and evaporating, when on cooling crystals of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ separate, which are neither efflorescent nor deliquescent. The solution has an alkaline reaction, owing to hydrolysis :



It has been used under the name of "tripsa" for softening boiler-water. The calcium bicarbonate is precipitated as carbonate by the alkali formed by hydrolysis, and calcium and magnesium chlorides and sulphates are precipitated as phosphates. The **hexametaphosphate** (p. 584) is now generally used in water-softening.

Sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ is obtained by heating the secondary phosphate (p. 582), and **sodium metaphosphate** NaPO_3 by heating the primary phosphate or microcosmic salt (p. 584).

Sodium sulphate.—Anhydrous sodium sulphate Na_2SO_4 occurs native as *thenardite*, and *glauberite* is the double salt $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$. The efflorescence on brick walls is usually sodium sulphate. Sodium sulphate is made as *salt-cake* in the first part of the Leblanc process (p. 210). It is also made by the *Hargreaves process* in which sulphur dioxide from pyrites burners, air and water vapour are passed over carefully moulded lumps of dry common salt heated in an iron retort, when the following reaction occurs :



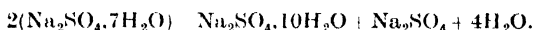
Sodium sulphate is also made from *kieserite* (p. 776) or magnesium sulphate in Stassfurt. This is dissolved in hot water and common salt added. On cooling, Glauber's salt crystallises, as it is the least soluble salt which can be formed from the ions Mg'' , Na' , SO_4'' and Cl' in the cold solution.

Sodium sulphate crystallises from water as *Glauber's salt* $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in large monoclinic prisms which effloresce readily in

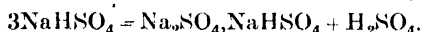
the air and fall to a white powder of the anhydrous salt. Glauber's salt is largely used in the textile industry and in small amounts as a purgative.

The crystals melt at $32\cdot38^\circ$ and at the same time deposit a white powder of the anhydrous solid salt, a solution saturated with the latter being formed. The solubility of Glauber's salt reaches a maximum at $32\cdot38^\circ$, since at this temperature the solid in contact with the solution is converted into the anhydrous salt, the solubility of which decreases with further rise of temperature. The solubility curve (see Fig. 53) consists of two parts meeting in a sharp angle at $32\cdot38^\circ$, the first being the solubility curve of Glauber's salt and the second that of the anhydrous salt.

Glauber's salt readily forms supersaturated solutions. If the supersaturated solution is brought in contact with a minute crystal of Glauber's salt, such as those floating in dusty air, crystallisation begins and Glauber's salt is deposited. But if cooled to 5° it deposits crystals of a metastable *heptahydrate* $\text{Na}_2\text{SO}_4\cdot7\text{H}_2\text{O}$, which become opaque when touched with a crystal of Glauber's salt owing to decomposition :



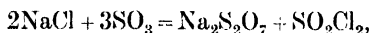
Sodium hydrogen sulphate NaHSO_4 (or "sodium bisulphate", $\text{Na}_2\text{O}\cdot2\text{SO}_3\cdot\text{H}_2\text{O}$) is formed in large prisms by cooling a solution of anhydrous sodium sulphate in warm concentrated sulphuric acid. It is formed in the preparation of hydrochloric acid (p. 209). It melts at a much lower temperature, $185\cdot7^\circ$, than the normal sulphate. A fused mixture or compound of this salt and the normal sulphate, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, is formed as a by-product in the manufacture of nitric acid and is known as *nitre-cake*. The hydrate $\text{NaHSO}_4\cdot\text{H}_2\text{O}$ is known. The solution of NaHSO_4 has an acid reaction : $\text{HSO}_4' \rightleftharpoons \text{SO}_4'' + \text{H}^+$. Sodium hydrogen sulphate is decomposed by alcohol into the salt $\text{NaHSO}_4\cdot\text{Na}_2\text{SO}_4$ and free sulphuric acid (dry KHSO_4 is not decomposed by dry alcohol) :



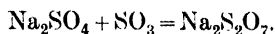
Sodium disulphate (or *pyrosulphate*) $\text{Na}_2\text{S}_2\text{O}_7$ is formed on moderate heating of the acid sulphate :



by the action of sulphur trioxide on common salt :



or (in the pure state) by the action of sulphur trioxide on the normal sulphate :



It melts at $400\cdot9^\circ$, and at a red heat it decomposes into sulphur trioxide and the normal sulphate.

Sodium in analysis.—Sodium compounds give a yellow flame coloration, which in the spectroscope shows two yellow lines very close together, known as the D-line. A yellow precipitate of sodium zinc uranyl acetate

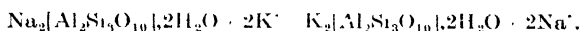
$\text{NaZn}_2(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_6$ is produced by zinc uranyl acetate* in neutral solution, from which potassium salts have been precipitated by zinc perchlorate. White sparingly soluble precipitates of sodium salts are formed with hydrofluosilicic acid, potassium antimonate, or potassium dihydroxytartrate, and fairly concentrated solutions of sodium compounds.

Sodium cyanide is made by the action of ammonia gas on a heated mixture of sodium and charcoal (*Castner's process*). Sodamide first formed reacts with carbon in two stages: (i) $2\text{NaNH}_2 + \text{C} \rightarrow \text{CN.NNa}_2$ (sodium cyanamide) + 2H_2 (at 300° – 600°); (ii) $\text{CN.NNa}_2 + \text{C} \rightarrow 2\text{NaCN}$ (at 700° – 800°). The fused cyanide obtained is cast into blocks.

POTASSIUM

Occurrence.—Potassium occurs much less accessibly than sodium, although it is widely distributed in the three kingdoms of nature.

Primary rocks often contain potassium silicate; granite contains about $2\frac{1}{2}$ per cent of potassium, mainly in the form of *orthoclase felspar* KAlSi_3O_8 . *Potash mica* or *muscovite* has the formula $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$. Felspar occurs in granite, gneiss and basalt, and mica in granite and gneiss. During the "weathering" of these rocks, *i.e.* their decomposition by atmospheric carbon dioxide and water, assisted by the disintegrating action of frost, the felspar is decomposed into clay and soluble potassium salts, such as potassium carbonate (p. 624). The potassium salts are retained by the soil, where they remain available for absorption by the roots of plants. The selective retention of potassium salts by the soil seems to depend on the exchange of potassium for sodium in *zeolites* (see p. 185) such as natrolite:



In plants, potassium occurs as salts of organic acids. When plants are burnt these organic salts form **potassium carbonate** K_2CO_3 , which (since it was formerly made by calcining cream of tartar) was called *salt of tartar*. Large amounts of potassium carbonate are made in Canada, Transylvania, and Russia by lixiviating wood ashes with water, evaporating the solution to dryness and calcining the residue in iron pots. The product is *pot-ash* and when purified is *pearl-ash*. Sugar beets absorb from the soil considerable amounts of potassium salts, which accumulate in the molasses known as *vinasse* or *schlempe*. This is evaporated on open hearths and splashed by paddles in the fire gases (Porion furnace); the syrup burns, leaving a residue of potassium carbonate. The vinasse may also be distilled in iron retorts, when methyl chloride and trimethylamine are formed.

The perspiration (*suint*) of sheep is rich in potassium salts. If raw wool is washed with water, the brown liquid evaporated and the residue calcined, about 5 parts of potassium carbonate remain per 100 of wool. This is a limited source of potassium salts.

Only small quantities of potassium salts occur in the sea and are absorbed in marine plants, from the ashes of which (*keelp*) they may be extracted.

* 10 gm. of uranyl acetate $\text{UO}_2\text{Ac}_2 \cdot 2\text{H}_2\text{O}$ and 6 ml. of acetic acid made up to 50 ml. form solution A. 30 gm. of zinc acetate $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ and 6 ml. of acetic acid made up to 50 ml. form solution B. Mix A and B and after 48 hours filter.

According to Dyer (1894), the minimum amount of soluble potash (K_2O) in a fertile soil is 0.01 per cent; the mean available potash content of British soils is 0.015 per cent. If successive crops are grown on the soil, the potassium compounds are removed and the soil becomes infertile. Trees remove annually 1.25 lb. of K_2O per acre, other plants more. In order to keep up the fertility of the soil, potassium compounds must be supplied and they are essential fertilisers.

The blood serum of all animals contains 0.022 per cent of potassium and 0.32 per cent of sodium. In the milk of carnivora, sodium and potassium occur in approximately equivalent amounts; in that of herbivora and in human milk, potassium predominates (3.5 : 1).

Although potassium compounds are widely distributed, *e.g.* as feldspar, comparatively few workable mineral deposits of salts occur. The principal are at Stassfurt in Saxony and near Mulhouse in Alsace, and in lesser amounts near Kalusz in Poland, Carlsbad in New Mexico, in Eastern Galicia, Searle's Lake (California), Cardona in Spain, Tunis, the Dead Sea (Palestine) and Elton Lake in the Urals.

The Alsatian and Galician deposits contain *sybivine* or *sybivinite*, a mixture of sodium and potassium chlorides. The Alsatian deposit consists of two strata, the upper with 35 to 40 per cent KCl and the lower with 24 to 32 per cent KCl.

The arrangement of the Stassfurt deposits (discovered in 1839 in boring for rock-salt) is as follows :

1. Upper layers, not containing potassium salts.
2. *Carnallite*, chiefly $KCl, MgCl_2, 6H_2O$.
3. *Kieserite*, chiefly $MgSO_4, H_2O$ —"Abraum" salts, *i.e.* above common salt.
4. *Polyhalite*, $2CaSO_4, MgSO_4, K_2SO_4, 2H_2O$.
5. *Kainite*, $MgSO_4, KCl, 3H_2O$.
6. Lower layers, not containing potassium salts.

The deposits were probably formed by the evaporation of an inland lake, as the order of the layers of salts is what would be expected in such a case (*van't Hoff*). The chief source of potassium salts at Stassfurt is the *carnallite* (see p. 699).

Potassium.—Metallic potassium can be made in a similar way to sodium by the electrolysis of fused potassium hydroxide, although the operation is difficult to carry out. It comes into the market in small spheres, kept under petroleum.

It may be obtained on a small scale by electrolysis of a fused mixture of equimolecular proportions of potassium chloride and calcium chloride in a porcelain crucible provided with two carbon electrodes, and heated with a Bunsen burner placed on the anode side, so that a solid crust forms over the cathode. A globule of potassium forms under the crust.

Metallic potassium was formerly made by strongly heating a mixture of the carbonate with charcoal in an iron bottle, and cooling the vapour rapidly in a flat iron condenser: $K_2CO_3 + 2C = 2K + 3CO$. Unless the

cooling is rapid, reaction of the potassium with carbon monoxide occurs, with the formation of a yellow compound $C_6O_6K_6$, which on exposure to moist air forms very explosive substances.

Potassium can be prepared by the electrolysis of potassium cyanide, by heating potassium hydroxide or sulphide with iron, magnesium, or aluminium, or by heating calcium carbide with potassium fluoride. The pure metal is best obtained by heating potassium chloride with calcium in a vacuum.

Potassium is a very light, soft metal, with a silver-white colour. It forms a green vapour. The metal is not acted upon by perfectly dry oxygen, but is rapidly corroded in moist air, becoming covered at first with a blue film. Potassium is chemically more energetic than sodium. Small pieces melt and take fire in air. It acts violently on water, the liberated hydrogen burning with a lilac-coloured flame. A fused globule of potassium hydroxide remains floating on the water; as it cools and touches the water, it explodes with a sharp crack. Heated potassium decomposes nearly every gas which contains oxygen; it also decomposes the oxides of boron and silicon, and the chlorides of magnesium and aluminium, on heating, with liberation of the elements.

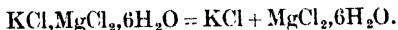
An alloy of sodium and potassium is liquid at room temperature and resembles mercury, but is very easily oxidised with evolution of heat and light on exposure to air. Potassium is feebly radioactive, the isotope ^{40}K emitting β -rays.

Potassium hydride.—Potassium hydride KH is a white crystalline solid formed by heating potassium in hydrogen. It ignites spontaneously in chlorine or oxygen; moist carbon dioxide at room temperature converts it into potassium formate:



Potassium chloride.—This salt KCl occurs in cubic crystals as *sylvine*. It is easily soluble in water, the solubility increasing almost linearly with temperature (*cf.* $NaCl$). It is made for use as a fertiliser from Stassfurt carnallite $KCl, MgCl_2, 6H_2O$.

The crude carnallite is heated with mother liquor containing magnesium chloride, when it dissolves. The solution is filtered and cooled, when crude potassium chloride crystallises out, leaving a mother liquor containing the magnesium chloride of the carnallite. The potassium chloride is then purified by washing and recrystallisation. When carnallite is fused, nearly pure potassium chloride separates, leaving fused magnesium chloride hexahydrate:

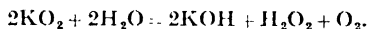


Potassium bromide KBr and **potassium iodide** KI are prepared as previously described (pp. 322, 331).

If hydrofluoric acid solution is neutralised with potassium hydroxide and the liquid evaporated in a platinum dish, cubic crystals of **potassium fluoride** KF are obtained. If to the neutralised liquid a further equal

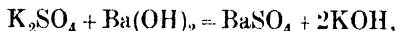
volume of hydrofluoric acid solution is added and the liquid evaporated in a platinum dish, crystals of potassium hydrogen fluoride KHF_2 or $\text{KF}\cdot\text{HF}$, called *Fremy's salt*, are obtained. This may be dried by gentle heating and is relatively stable. On heating more strongly it decomposes: $\text{KHF}_2 = \text{KF} + \text{HF}$. The salts KH_2F_3 and KH_3F_4 are also known.

Oxides of potassium.—Potassium monoxide K_2O is light yellow and is prepared in a similar way to the sodium compound and has similar properties. Potassium dioxide KO_2 is a chrome-yellow solid formed by burning the metal in oxygen or air. It oxidises carbon monoxide to dioxide below 100° , and is decomposed by water:



The common higher oxide of potassium is KO_2 , that of sodium is Na_2O_2 . On heating KO_2 in vacuum it first forms K_2O_3 and then K_2O_2 .

Potassium hydroxide (*caustic potash*) is prepared in a similar way to sodium hydroxide, which it resembles closely in its properties. It is made on the large scale by the electrolysis of potassium chloride solution and is used in the manufacture of *soft soap* (potassium salts of oleic, palmitic and stearic acids). The pure hydroxide is best prepared by adding powdered potassium sulphate to a hot saturated solution of barium hydroxide:



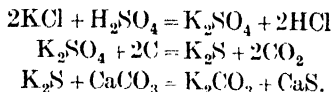
or by the action of water on potassium amalgam. The solutions attack glass, and should be decanted (not filtered) and evaporated in silver, nickel or iron dishes. Platinum is attacked by fused alkalis.

Potassium hydroxide is more soluble than sodium hydroxide both in water and in alcohol, and the alcoholic solution ("alcoholic potash") is used as a reagent; it becomes brown owing to oxidation of the alcohol. Potassium hydroxide forms a crystalline hydrate $\text{KOH}\cdot 2\text{H}_2\text{O}$, m. pt. $35\cdot 5^\circ$, although solutions containing more than 85 per cent deposit KOH on cooling.

The impure commercial potassium hydroxide containing chloride, carbonate and sulphate may be purified by dissolving in alcohol, decanting from the impurities, evaporating the solution in a silver dish and fusing the residue. It is sold as "pure by alcohol" but may contain a little potassium acetate formed from the alcohol, and potassium nitrite if nitrate was added to purify the potassium hydroxide (see p. 691).

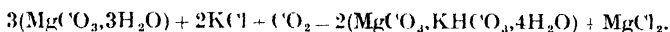
Potassium borates.—Several potassium borates are described. Potassium metaborate KBO_2 is prepared by fusing potassium carbonate with B_2O_3 ; on adding potassium hydroxide to boric acid till the solution is alkaline, a diborate which crystallises as $\text{K}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$ is formed. By mixing H_3BO_3 and $2\text{K}_2\text{CO}_3$ in hot solutions, a triborate $2\text{KB}_3\text{O}_5\cdot 5\text{H}_2\text{O}$ is formed, whilst the pentaborate $\text{KB}_5\text{O}_8\cdot 4\text{H}_2\text{O}$ is made by saturating hot potassium hydroxide solution with boric acid and cooling.

Potassium carbonate.— K_2CO_3 is extracted from wood-ash (p. 697), and when purified is called *pearl-ash*. It can be made from potassium chloride by a modification of the Leblanc process; the chloride is first decomposed with sulphuric acid to form potassium sulphate as in the salt-cake process, and the sulphate is then heated with coal and limestone as in the black-ash process:

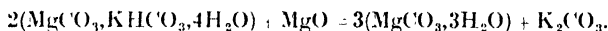


Potassium carbonate is usually made from potassium chloride by the **Precht process**.

A concentrated solution of potassium chloride is mixed with solid hydrated magnesium carbonate $MgCO_3 \cdot 3H_2O$, and carbon dioxide (limekiln gas) is passed into the suspension. A solid compound of potassium bicarbonate and magnesium carbonate is precipitated and a solution of magnesium chloride is formed:



The solid double carbonate is then stirred with water and magnesium oxide at 40° , when a solution of potassium carbonate and a residue of hydrated magnesium carbonate are formed:

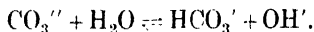


The solution of potassium carbonate is filtered and evaporated.

Potassium carbonate is a white deliquescent solid, very easily soluble in water to form a solution which is strongly alkaline on account of hydrolysis:



or

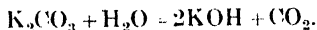


One hundred parts of water dissolve:

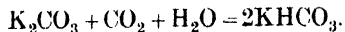
Temp.	0°	26°	40°	60°	90°	135° (b. pt. sat. sol.)
K_2CO_3	105	113.5	117	127	140	205

The concentrated solution on standing deposits monoclinic crystals of $2K_2CO_3 \cdot 3H_2O$, and below 6° the hydrate $K_2CO_3 \cdot 6H_2O$ crystallises.

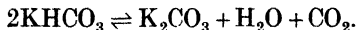
Potassium carbonate melts at 900° and it forms a more easily fusible mixture ("fusion mixture") with sodium carbonate. It is decomposed by steam at a red heat:



A saturated solution of potassium carbonate absorbs carbon dioxide and deposits monoclinic crystals of potassium hydrogen carbonate (*bicarbonate*):

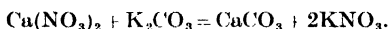


Potassium hydrogen carbonate is easily made by passing carbon dioxide over moist potassium carbonate and drying on a porous plate. It is much less soluble in water than the normal carbonate, but is more soluble than sodium bicarbonate. The recrystallised bicarbonate may be used in preparing pure potassium carbonate, since it decomposes on heating at 190° :



Potassium nitrate KNO_3 , called *nitre* or *saltpetre* (Latin, *sal petrae*), may be prepared by neutralising dilute nitric acid with potassium hydroxide or carbonate, evaporating and crystallising. It is manufactured for use in making gunpowder, and small amounts are also used in pickling meat, e.g. hams. An old method of manufacturing saltpetre which is still used in India and Egypt is in the so-called *nitre plantations*.

Soil containing decomposing nitrogenous organic matter such as urine is mixed with lime or calcium carbonate, such as old mortar, when calcium nitrate $\text{Ca}(\text{NO}_3)_2$ is formed, probably from the oxidation of ammonia formed by the decomposition of organic matter in the presence of feeble alkalis, by the activity of micro-organisms present in soil (see p. 533). The material is lixiviated and a solution containing calcium nitrate is obtained which is boiled with wood-ashes (containing potassium carbonate) :



The filtrate on evaporation deposits saltpetre, which is purified by recrystallisation.

The cheaper sodium nitrate (Chile saltpetre) is converted into potassium nitrate by dissolving potassium chloride in a little hot water and adding sodium nitrate. Sodium chloride, the least soluble salt formed from the four ions K^+ , Na^+ , NO_3^- , Cl^- , deposits from the hot liquid, since its solubility is not much increased by rise of temperature (see Fig. 53) ; the filtered liquid is cooled, when potassium nitrate crystallises, since it is the least soluble salt at lower temperatures. It is recrystallised from water.

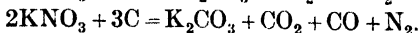
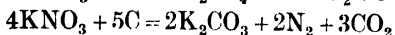
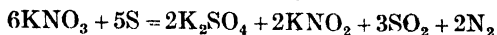
The process may be illustrated by dissolving 11.5 gm. of NaNO_3 and 10 gm. of KCl in 10 ml. of boiling water ; white granular NaCl remains ; on filtering through a hot-water funnel, the filtrate on cooling deposits crystals of KNO_3 , which may be recrystallised.

Potassium nitrate usually crystallises in large anhydrous rhombic prisms, but if the solution is slowly evaporated on a watch-glass, rhombohedra isomorphous with sodium nitrate and with calcite are deposited. Nitre melts at 336° and at a higher temperature evolves oxygen :



The fused salt is a powerful oxidising agent : sulphur, charcoal and

phosphorus take fire on it and burn brilliantly, with the formation of potassium sulphate, carbonate and phosphate :



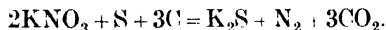
Potassium chlorate is a more powerful oxidising agent than potassium nitrate.

Potassium nitrite KNO_2 is made in the same way as sodium nitrite (p. 551).

Gunpowder.—Most of the potassium nitrate of commerce is used in making gunpowder.

This was apparently first made by the Chinese about 1150 A.D. if not earlier, for the production of fireworks. *Greek fire*, used in the Byzantine period, was a mixture of salt, resin, quicklime, pitch and sulphur, although some kinds may have contained saltpetre. The invention of gunpowder in the West is usually credited to Roger Bacon (1214–1292), who in his *De secretis operibus artis et de nullitate magiae*, probably composed about 1248, mentions saltpetre and sulphur as constituents but conceals charcoal in an anagram. The full recipe is given in the *Liber Ignium* of Marcus Græceus, the earliest MSS. of which are practically contemporary with Bacon ; it also gives recipes for “liquid fire” for military purposes. Firearms seem to have been used in Florence in 1325, but field pieces were first employed by the English in the battle of Crécy in 1346.

Gunpowder is an intimate mixture of finely powdered nitre, wood-charcoal (carbonised at a low temperature) and sulphur, the materials being ground and incorporated under stone rollers. The proportions of the constituents and the main products of combustion correspond roughly with the equation :



The proportions of nitre, carbon and sulphur corresponding with this equation are 75, 13 and 12, respectively. Carbon monoxide is also evolved in the explosion and the residue contains some potassium carbonate and sulphate. Abel and Noble (1875) considered that the explosion of gunpowder cannot adequately be represented by a chemical equation, since the reactions are complicated.

The gaseous product is mostly carbon dioxide, carbon monoxide and nitrogen, whilst the solid product (including that in the dense smoke) is mainly potassium carbonate, potassium sulphate and potassium sulphide.

Potassium cyanide.—Potassium cyanide is formed by heating potassium ferrocyanide at a bright red heat : $\text{K}_4\text{Fe}(\text{CN})_6 = 4\text{KCN} + \text{Fe} + 2\text{C} + \text{N}_2$, or with potassium carbonate : $\text{K}_4\text{Fe}(\text{CN})_6 + \text{K}_2\text{CO}_3 = 5\text{KCN} + \text{KCNO} (\text{cyanate}) + \text{CO}_2 + \text{Fe}$. If the ferrocyanide is fused with sodium,

a mixture of sodium and potassium cyanides is formed : $K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe$. Potassium cyanide is prepared by **Beilby's process** ; ammonia gas is passed over a mixture of fused potassium carbonate and carbon : $K_2CO_3 + C + 2NH_3 = 2KCN + 3H_2O$. The fused cyanide is decanted and moulded, and is pure.

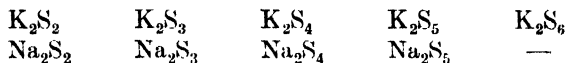
Very pure potassium cyanide, m. pt. 634.5° , is obtained by recrystallising from anhydrous liquid ammonia. **Potassium cyanate** $KCNO$ is made by fusing the cyanide with lead oxide : $KCN + PbO = KCNO + Pb$, or by heating potassium ferrocyanide and potassium dichromate in an iron dish, and extracting with 80 per cent alcohol. The aqueous solution slowly hydrolyses with formation of ammonia : $KCNO + 2H_2O - NH_3 + KHCO_3$. When acidified it evolves carbon dioxide with effervescence : $HCNO + H_2O = CO_2 + NH_3$.

Potassium thiocyanate $KCNCS$, m. pt. 161° , is formed by fusing a mixture of potassium ferrocyanide and carbonate with sulphur. It occurs in traces in saliva. **Potassamide** KNH_2 (m. pt. 271°), is formed by passing dry ammonia gas over heated potassium : $2K + 2NH_3 = 2KNH_2 + H_2$.

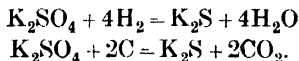
Potassium phosphates.—The common potassium phosphate is **primary potassium phosphate** (potassium dihydrogen phosphate) KH_2PO_4 , which is formed in crystals from a solution of the requisite amounts of phosphoric acid and potassium hydroxide. The **secondary potassium phosphate** K_2HPO_4 (corresponding with ordinary sodium phosphate) is very difficult to crystallise. The **tertiary potassium phosphate** K_3PO_4 is made by crystallising from a solution containing an excess of potassium hydroxide, and is very soluble. **Potassium pyrophosphate** $K_4P_2O_7$, and several forms of the metaphosphate $(KPO_3)_n$ are known. A **potassium phosphide** K_2P_5 is formed by heating the elements at 400° in a vacuum tube (Na_2P_5 , Rb_2P_5 , and Cs_2P_5 are obtained similarly).

Potassium and sodium sulphides.—Potassium and sodium burn when heated in sulphur vapour, forming mixtures of sulphides. By using excess of metal and heating the product in a vacuum, the pure monosulphides K_2S and Na_2S remain in cubic crystals.

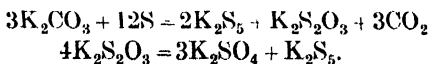
The freezing points of mixtures of the monosulphides and sulphur show that the following higher sulphides exist :



The **monosulphides** Na_2S and K_2S are obtained by passing hydrogen over the heated sulphates, and less pure by heating the sulphates with excess of carbon :

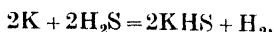


By fusing potassium carbonate with sulphur, a liver-coloured mass is obtained, called *liver of sulphur* (*hepar sulphuris*). It contains polysulphides of potassium and potassium sulphate : the pentasulphide and thiosulphate are first formed but most of the thiosulphate is decomposed by heat :

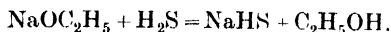


A solution of liver of sulphur is used in gardening to combat mildew and insect pests.

If a solution of potassium or sodium hydroxide is saturated with hydrogen sulphide and evaporated, the hydrosulphides $\text{NaHS}\cdot 2\text{H}_2\text{O}$ or $\text{NaHS}\cdot 3\text{H}_2\text{O}$, and $2\text{KHS}\cdot \text{H}_2\text{O}$ crystallise. The anhydrous hydrosulphides are obtained by heating the metals in hydrogen sulphide :

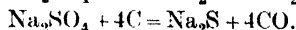
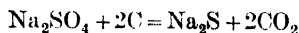


or by the action of hydrogen sulphide on solutions of sodium or potassium ethoxides in ethyl alcohol :

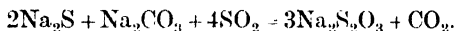


If a solution of potassium or sodium hydroxide is saturated with hydrogen sulphide, an equal volume of the alkali is added, and the solution is evaporated, the monosulphides $\text{K}_2\text{S}\cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ separate in colourless crystals.

Sodium sulphide is made technically by fusing sodium sulphate (salt-cake) with powdered coal in a revolving furnace :



The product is lixiviated with water, evaporated and crystallised. It is used in removing hair from skins and in making sulphur dyes. The residual sulphide liquor is treated with sodium carbonate and sulphur dioxide to make sodium thiosulphate :



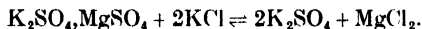
By boiling alcoholic solutions of the hydrosulphides with sulphur, potassium pentasulphide K_2S_5 and sodium tetrasulphide Na_2S_4 are obtained. K_2S_5 forms bright orange-red crystals giving a deep-orange solution which becomes darker on heating. Na_2S_4 forms dark-yellow crystals giving a deep-orange solution which also becomes darker on heating. Sodium disulphide Na_2S_2 is obtained by adding sodium to an alcoholic solution of Na_2S_4 and forms bright-yellow microscopic crystals, giving a deep-yellow solution which does not darken on heating.

Potassium sulphate.—When dilute sulphuric acid is neutralised with potassium hydroxide or carbonate and the solution evaporated, anhydrous rhombic prisms of potassium sulphate K_2SO_4 separate. These are not very soluble in water (10.3 gm. at 15° and 24.1 gm. at 100° in 100 gm. of water); the solubility increases almost linearly with the temperature (Fig. 53).

Potassium sulphate occurs in large quantities in the Stassfurt potash deposits as double salts: *schönite* $\text{K}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 6\text{H}_2\text{O}$, and *kainite* $\text{K}_2\text{SO}_4\cdot\text{MgSO}_4\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$.

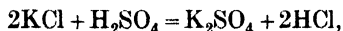
If kainite is dissolved in hot water it breaks up into its constituent ions K^+ , Mg^{++} , SO_4^{--} , Cl^- . By fractional crystallisation, those salts separate first (including double salts) with which the solution first becomes saturated (van't Hoff). From warm solutions the double salt *schönite* first separates,

since it is least soluble, and magnesium chloride remains in solution. If the schönite is digested with a solution of potassium chloride (occurring at Stassfurt as *sylvine*), the following reaction occurs :



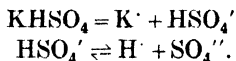
The sparingly soluble potassium sulphate separates first, followed by *carnallite* $\text{KCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$, from which potassium and magnesium chlorides can be prepared.

Potassium sulphate is made in smaller amounts by heating potassium chloride with concentrated sulphuric acid :



and as a by-product in the manufacture of potassium dichromate and permanganate. It is used in the preparation of potash alum and as a fertiliser, especially for tobacco, since it is not easily fusible (m. pt. 1050°) and gives a suitable ash.

When potassium sulphate is heated with an equivalent amount of concentrated sulphuric acid it dissolves, forming **potassium hydrogen sulphate** KHSO_4 ("potassium bisulphate" $\text{K}_2\text{O}, 2\text{SO}_3, \text{H}_2\text{O}$ or "acid potassium sulphate") (Roullé, 1754). This is easily fusible and solidifies on cooling. It is obtained as a by-product in the laboratory preparation of nitric acid. It is readily soluble in water, the solution having a strongly acid reaction :



On evaporation the solution (in accordance with van't Hoff's rule) deposits the normal sulphate K_2SO_4 , which is the salt with which it first becomes saturated. The residual solution contains free sulphuric acid. From it on cooling the compound $\text{K}_2\text{SO}_4, \text{KHSO}_4$ deposits, and finally KHSO_4 . The compounds $\text{K}_2\text{SO}_4, 3\text{KHSO}_4$ and $\text{K}_2\text{SO}_4, 6\text{KHSO}_4$ are also known.

At a red heat potassium hydrogen sulphate loses water and forms **potassium disulphate** :



At higher temperatures this evolves sulphur trioxide :



It is used to attack refractory minerals in analysis, since it behaves like sulphuric acid of high boiling point. Thus chromite FeCr_2O_4 is converted into ferrous and chromic sulphates, FeSO_4 and $\text{Cr}_2(\text{SO}_4)_3$, although it is not attacked by boiling sulphuric acid. Since loss of water on heating KHSO_4 is incomplete even in a vacuum, the pure disulphate is best obtained from sulphur trioxide and potassium sulphate :



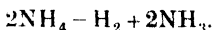
Potassium in analysis.—Potassium salts form sparingly soluble salts with perchloric, hydrofluosilicic, chloroplatinic, phosphotungstic, tartaric and

picric acids, and with sodium cobaltinitrite. Potassium iodide is not precipitated by chloroplatinic acid. Potassium hydrogen tartrate is precipitated only in solutions containing no mineral acid; it (as well as the chloroplatinate) is precipitated more easily by adding alcohol and scratching the tube with a glass rod. The lilac flame coloration and the spectrum are also useful as tests.

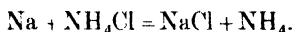
AMMONIUM

Ammonium amalgam.—Ammonia readily combines with acids to form salts. Lavoisier, and later Dumas (1828), regarded these as compounds of ammonia with acids, *e.g.* ammonia hydrochloride $\text{NH}_3\cdot\text{HCl}$. Davy (1808) and Ampère (1816) supposed that the salts contain the ammonium radical NH_4 , which behaves like an alkali-metal. Sal ammoniac is *ammonium chloride* NH_4Cl , analogous to potassium chloride KCl . This view was favoured by Berzelius in 1820.

The ammonium theory was supported by the discovery of ammonium amalgam independently in 1808 by Seebeck in Jena and by Berzelius and Pontin in Stockholm. If a solution of ammonium chloride is electrolysed with a mercury cathode (Fig. 136) the mercury swells up, forming a soft pasty mass which rapidly decomposes, evolving hydrogen and ammonia in the ratio of 1 vol. to 2 :



Davy in 1808 confirmed this observation and showed that ammonium amalgam is also formed by the action of potassium or sodium amalgam on a solution of ammonium chloride :

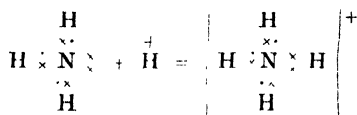


If a little sodium amalgam is added to a cold concentrated solution of ammonium chloride, the amalgam swells up to a spongy mass. If this is put into water, bubbles of hydrogen are evolved and the liquid smells of ammonia.

Seely (1870) found that ammonium amalgam compressed in a tube under a piston obeys Boyle's law and concluded that it was simply a froth of hydrogen and ammonia gases in mercury. Ammonia, however, is very soluble in water and other experiments favour the existence of ammonium in the amalgam. Although the amalgam does not reduce solutions of ferric chloride or copper sulphate at the ordinary temperature, it reduces solutions of copper, cadmium, zinc, and even barium, salts at 0° . The voltage required to deposit sodium on a mercury cathode is similar to that required in the formation of ammonium amalgam. Ammonium amalgam is also formed by the action of sodium amalgam on ammonium chloride dissolved in anhydrous liquid ammonia. The deep-blue solutions obtained by dissolving sodium or potassium in liquid ammonia may contain metal ammoniums NH_2Na and NH_2K .

According to Schlubach and Ballauf (1921) a colourless solution containing free ammonium is formed by adding the blue solution of sodium in liquid ammonia to a solution of ammonium iodide in the same solvent, at 70° : $\text{Na} + \text{NH}_4\text{I} = \text{NH}_4 + \text{NaI}$. It decomposes at -40° : $2\text{NH}_4 = 2\text{NH}_3 + \text{H}_2$.

The ammonium ion.—The ammonium salts were once thought to contain 5-valent nitrogen, e.g. $(H_4)\equiv N-Cl$, but it is now considered that the positive ammonium ion is formed by the addition of the neutral ammonia molecule to the hydrogen ion (proton), which remains univalent so that the whole ammonium ion is also univalent. The proton is linked by the lone pair of electrons on the nitrogen atom :



The four hydrogens are attached to the nitrogen at the corners of a tetrahedron with nitrogen at the centre, as is proved by the optical activity of a spiran compound (Fig. 360), the tetrahedral arrangement of valencies being necessary to form a dissymmetric structure (Mills and Warren, 1925). In ammonium salts the NH_4 ions form a lattice with negative ions.

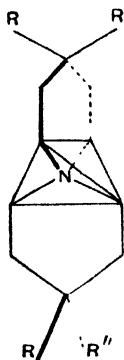
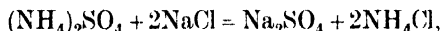


FIG. 360.—Tetrahedral structure of the ammonium ion.

Ammonium chloride NH_4Cl (*sal ammoniac*) occurs in volcanic gases. It is prepared by neutralising ammonia with hydrochloric acid and evaporating, also by subliming a mixture of ammonium sulphate with common salt :

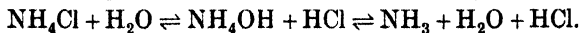


by heating in a cast-iron basin provided with an iron dome having a small hole at the top. The cake of ammonium chloride which sublimes into the dome is broken up and forms tough fibrous irregular lumps, often stained in yellow patches with ferric chloride. An imitation of the sublimed product is made by strongly compressing the powdered salt: *voltoids*, used in batteries, are small tablets prepared by compression.

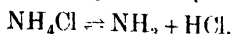
Ammonium chloride is made in ammonia-soda works by crystallising the liquors from the bicarbonate filters (p. 692), which contain NH_4Cl , $NaCl$ and $CaCl_2$, and drying the salt with hot air.

Ammonium chloride crystallises in feathery growths which are aggregates of small octahedra or other forms of the regular system, but the crystals look like crystals of the hexagonal or tetragonal system. From a solution containing urea it crystallises in cubes. There are two forms with a transition point at 184.5° .

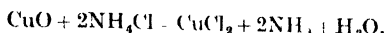
Ammonium chloride is readily soluble in water and a considerable lowering of temperature results. It is very sparingly soluble in absolute alcohol. The aqueous solution is only slightly hydrolysed and is neutral, but ammonia escapes on boiling, leaving a distinctly acid liquid :



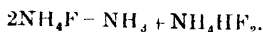
Ammonium chloride vapour is practically completely dissociated :



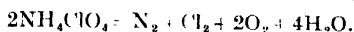
According to H. B. Baker, when the pure salt is carefully dried over P_2O_5 , it gives the normal vapour density corresponding with NH_4Cl , but this result was called in question by Rodebush and Michalek (1929), who used an impure salt. The dissociation on heating explains the action of ammonium chloride as a flux in soldering: the metallic oxides are converted into volatile chlorides by the hydrochloric acid, and a clean metal surface is left, e.g.:



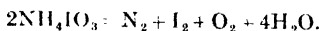
Ammonium fluoride NH_4F , bromide NH_4Br , and iodide NH_4I are obtained by neutralising the corresponding acids with ammonia. The fluoride decomposes on fusion to form the acid fluoride:



Ammonium chlorate NH_4ClO_3 is unstable and spontaneously explosive; even solutions may explode violently on evaporation. Ammonium perchlorate NH_4ClO_4 is more stable, but is endothermic and deliquesces with a yellow flame over 200° :

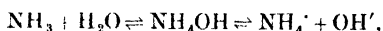


Ammonium iodate decomposes on heating:

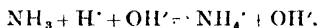


Ammonium hydroxide.—Although crystalline solid $2\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ are known (p. 516), it is doubtful if they are ammonium oxide $(\text{NH}_4)_2\text{O}$ and ammonium hydroxide NH_4OH , respectively.

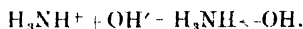
It is sometimes supposed that aqueous ammonia contains ammonium hydroxide, which is a weak base:



but its general properties can be explained by supposing that the ammonia withdraws hydrogen ions from the water to form ammonium ions, leaving the hydroxyl ions of the water which cause the alkaline reaction:



Ammonia is a weak base and this has been explained by supposing that the lone pair of electrons on the hydroxyl oxygen can co-ordinate with a hydrogen of the ammonium ion to form unionised ammonium hydroxide



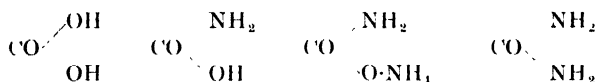
A quaternary ammonium hydroxide, e.g. tetramethyl ammonium hydroxide $(\text{CH}_3)_4\text{N} \cdot \text{OH}$, is a strong base since its radical has no hydrogen with which the hydroxyl oxygen can co-ordinate: $(\text{CH}_3)_4\text{N}^+ + \text{OH}^-$.

Ammonium carbonates.—Commercial ammonium carbonate or *sal volatile* is made by heating a mixture of chalk and sal ammoniac or ammonium sulphate in an iron retort with a lead receiver, into which the salt sublimes. The product is resublimed after addition of a little water, and forms a white semi-transparent fibrous mass covered on the

outside with a white opaque powder of **ammonium bicarbonate** NH_4HCO_3 , and smelling strongly of ammonia.

This commercial carbonate is a compound of the bicarbonate and **ammonium carbamate** $\text{NH}_4\text{O}\cdot\text{CO}\cdot\text{NH}_2$, with some normal carbonate $(\text{NH}_4)_2\text{CO}_3$.

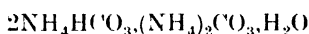
Carbamic acid is the monoamide of carbonic acid, the diamide being urea (*carbamide*):



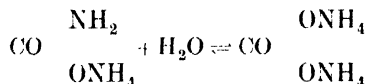
If commercial ammonium carbonate is treated with alcohol the carbamate dissolves leaving the bicarbonate; on exposure to air the carbamate slowly volatilises, leaving the bicarbonate as a white powder. The bicarbonate can be crystallised: it decomposes at 60° :



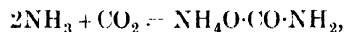
although at the ordinary temperature it does not smell of ammonia. Commercial ammonium carbonate can be used as a baking powder since it volatilises completely on heating. If it is gently warmed with concentrated ammonia solution **ammonium sesquicarbonate**



is obtained in crystals. The normal carbonate $(\text{NH}_4)_2\text{CO}_3$ is obtained by digesting *sal volatile* for two hours with concentrated ammonia at 12° , and drying between filter-paper the crystalline powder remaining, which is $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$. It is formed when the carbamate is dissolved in water:



so that when the commercial carbonate is dissolved in ammonia solution the normal carbonate is formed. The carbamate is deposited when 2 vols. of ammonia gas and 1 vol. of CO_2 are mixed:



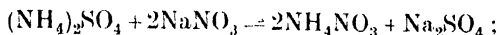
and on heating it dissociates into these gases.

Synthetic **urea** is made by heating a mixture of ammonia gas, carbon dioxide and a little water under pressure at 135° ; ammonium carbamate is first formed and then loses water:

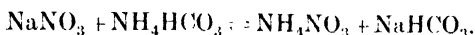


Ammonium nitrate NH_4NO_3 was first prepared by Glauber and called *nitrum flammans* (it explodes when suddenly heated). It is made by neutralising nitric acid with ammonia or ammonium carbonate. On the large scale it is made: (1) by passing ammonia gas

into 60 per cent nitric acid; (2) by the double decomposition of calcium nitrate and ammonium carbonate or sulphate in solution; (3) by the double decomposition of ammonium sulphate and sodium nitrate in solution:



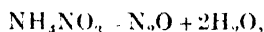
(4) by using sodium nitrate instead of common salt in the ammonia-soda process:



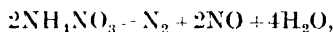
Another method of preparation is described on p. 541.

Ammonium nitrate exists in five crystalline forms, with definite transition temperatures: tetragonal -17° ; rhombic-I 32.1° ; rhombic-II 84.2° ; rhombohedral 125.2° ; cubic 169.6° ; liquid. The melting point of the anhydrous salt is 169.6° , that of the ordinary salt containing a little moisture is 165° . The transition at 84.2° is accompanied by an expansion which may break a glass vessel in which the salt has solidified.

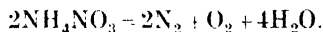
Ammonium nitrate is used in the preparation of nitrous oxide (p.546):



and as a constituent of explosives. It deflagrates with a yellow flame above 250° :



and at higher temperatures it detonates:



A mixture (*amatol*) of 80 parts of ammonium nitrate and 20 parts of trinitrotoluene is used as an explosive.

Ammonium nitrite NH_4NO_2 is obtained as an explosive deliquescent solid by passing " N_2O_3 " gas (p. 549) over solid ammonium carbonate in a cooled tube, dissolving in alcohol, and precipitating with ether (Sörensen, 1894).

It can also be prepared by evaporating a concentrated solution of sodium nitrite and ammonium chloride in vacuum and subliming in vacuum (Neogi and Adhicary, 1911).

A solution for the preparation of nitrogen is made by mixing sodium nitrite with ammonium chloride or sulphate in solution.

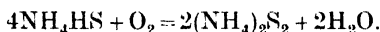
The **ammonium phosphates** $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ are formed from ammonia and phosphoric acid. The salt $(\text{NH}_4)_2\text{HPO}_4$ crystallises when a solution containing an excess of ammonia is allowed to evaporate. *Microcosmic salt* $\text{NaNH}_4\text{HPO}_4$ is described on p. 695.

Ammonium sulphides.—The formation of colourless needles and plates of **ammonium hydrosulphide** NH_4HS by mixing equal volumes of viscous ammonia and hydrogen sulphide was described by Bineau (1838) and confirmed by Bloxam (1893).

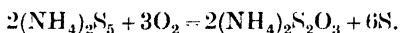
Bineau (1839) stated that a mixture of 2 vols. of ammonia with 1 vol. of hydrogen sulphide at -18° gave mica-like crystals of ammonium monosulphide $(\text{NH}_4)_2\text{S}$, but Bloxam found that these crystals always contain ammonium hydrosulphide, and although he says he obtained the monosulphide by carefully adjusting the volumes of the reacting gases and their rates of flow, the product was probably contaminated with hydrosulphide (Thomas and Riding, 1923).

Pure ammonium hydrosulphide is precipitated in fine needles on passing dry ammonia and dry hydrogen sulphide alternately into dry ether. It dissociates rapidly and can be kept only in sealed vessels.

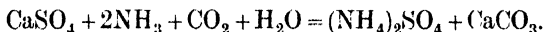
When hydrogen sulphide is passed into concentrated (0.880) ammonia solution diluted with four times its volume of water, a solution of the hydrosulphide is formed (Kirwan, 1786). Crystals of $(\text{NH}_4)_2\text{S} \cdot 2\text{NH}_4\text{HS}$ separate on cooling to 0° a solution prepared by saturating 0.880 ammonia with hydrogen sulphide. The normal sulphide does not appear to exist in solution. The freshly prepared solution of the hydrosulphide is colourless, but rapidly oxidises on exposure to air and becomes yellow owing to liberation of sulphur, which dissolves in the excess of hydrosulphide to form yellow ammonium polysulphides $(\text{NH}_4)_2\text{S}_x$:



The same *yellow ammonium sulphide* is obtained by digesting flowers of sulphur with the solution of the hydrosulphide: the main product appears to be $(\text{NH}_4)_2\text{S}_5$. On prolonged exposure to air the solution deposits sulphur, and forms a colourless solution containing ammonium thiosulphate:



Ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, described by Libavius (1597), is manufactured by passing ammonia gas into 60 per cent sulphuric acid (p. 521). Instead of using sulphuric acid, ammonia gas may be absorbed in a suspension of calcium sulphate (calcined gypsum) and carbon dioxide passed into the liquid, when calcium carbonate is precipitated and a solution of ammonium sulphate is formed:



Ammonium sulphate forms large transparent crystals isomorphous with potassium sulphate and very soluble in water. On heating powdered ammonium sulphate it loses ammonia even below 100° , and at 300° is completely converted into molten ammonium hydrogen sulphate which melts at 140° after solidification:



At higher temperatures, decomposition with evolution of sulphur dioxide and nitrogen occurs. The acid sulphate is also obtained in deliquescent crystals by dissolving the normal sulphate in hot concentrated sulphuric acid and cooling.

Ammonium sulphite $(\text{NH}_4)_2\text{SO}_3$ crystallises on cooling a solution of sulphur dioxide in excess of concentrated ammonia solution.

Alkali metal polyhalides.—Iodine is more soluble in alkali iodide solution than in water, and the brownish-red solution contains the tri-iodide ion I_3^- . Many *solid* polyiodides and mixed halides are known, mostly anhydrous but potassium tri-iodide only as the hydrate $\text{KI}_3 \cdot \text{H}_2\text{O}$. The methods of preparation include (i) the direct addition of halogen ($\text{KICl}_2 + \text{Cl}_2 = \text{KICl}_4$), and (ii) halogen or halogen compound displacement ($\text{CsBr}_3 + \text{I}_2 = \text{CsIBr}_2 + \text{IBr}$; $\text{CsICl}_2 + 2\text{I}_2 = \text{CsI}_2\text{Cl} + 2\text{ICl}$). Apart from the actual preparation of the solids, the complex ions may be detected in solution.

In a method used by Abegg and Hamburger (1906) a fairly concentrated solution of iodine in benzene is shaken with solid alkali iodide MI . If two *solid* phases are present, e.g. MI_x and MI , the iodine concentration in the liquid phase will be constant on addition of iodine until there is only one solid phase MI_x , when it begins to alter. The solid is analysed at this point.

Some types of polyhalides are :

- (1) MX_2 : known only as $\text{NaI}_2 \cdot 3\text{H}_2\text{O}$.
- (2) MX_3 : a common type, known in tri-iodides of K (hydrated), Rb, Cs, NH_4 , Tl; tribromides RbBr_3 , CsBr_3 ; and mixed halides MICl_2 (K, Rb, Cs, NH_4), CsI_2Cl (the only one of this type), CsIBr_2 , KIBrCl , CsIBrF , etc.
- (3) MX_4 : known as $\text{NaI}_4 \cdot 2\text{H}_2\text{O}$ and CsI_4 (which may be Cs_2I_8).
- (4) MX_5 : known in $\text{NaI}_5 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, and the very stable orange-red mixed halides MICl_4 (Li, Na, K, Rb, Cs, NH_4), also MICl_3F .
- (5) MI_6 : known in $2\text{KBr}_6 \cdot 3\text{H}_2\text{O}$.

In these compounds the heavy halogen is multivalent, the $[\text{Cl}-\text{I}-\text{Cl}]^-$ ion being linear and the ICl_4^- ion square with four chlorine atoms at the corners.

LITHIUM

Lithium is widely distributed, but occurs in quantity only in a few rare minerals. Traces of lithium are found in milk, blood, plants (especially tobacco), and the soil. The lithium minerals are *triphylite* $(\text{Li}, \text{Na})_3\text{PO}_4 + (\text{Fe}, \text{Mn})_3(\text{PO}_4)_2$ (1.6-3.7 per cent Li), *petalite* $\text{LiAl}(\text{Si}_2\text{O}_5)_2$ (2.7-3.7 per cent Li), *lepidolite* or *lithium mica* $(\text{Li}, \text{K}, \text{Na})_2\text{Al}_2(\text{SiO}_3)_4(\text{F}, \text{OH})_2$, *amblygonite* $\text{Li}(\text{F}, \text{OH})\text{AlPO}_4$ (2.4-3 per cent Li), and *spodumene* $\text{LiAl}(\text{SiO}_3)_2$ (3.8-5.6 per cent Li). Lithium occurs in some mineral springs, e.g. in Baden and at Redruth in Cornwall, in some radioactive minerals (e.g. carnotite), and in the sea. Traces of lithium are found in many minerals and in most kinds of glass.

Lithium was discovered by Arfvedson (1817) in petalite and spodumene; the metal was isolated by Bunsen and Matthiessen in 1855 by the electrolysis of the fused chloride. Lithium may also be obtained by the electrolysis of lithium bromide containing 10 per cent of lithium chloride. It is a silver-white metal, harder than sodium, tarnishing in the air, although less readily than the other alkali-metals, and decomposing water with evolution

of hydrogen. It is the lightest metal (density 0.53 at 20°). It does not fuse on water like sodium and potassium, since its melting point (180°) is higher.

Lithium salts are extracted from the minerals, such as spodumene, in various ways. In one process the finely-powdered mineral is digested with concentrated sulphuric or hydrochloric acid, which is evaporated to render silica insoluble. The residue is taken up with water and the solution filtered. To the filtrate the requisite amount of sodium carbonate is added to precipitate iron, alumina, magnesia, etc., and the filtrate is concentrated by evaporation. Excess of sodium carbonate is then added, when **lithium carbonate** Li_2CO_3 is precipitated, as it differs from other alkali carbonates in being sparingly soluble in water. Another process is to fuse the mineral with barium carbonate and sulphate, extract with water, precipitate the filtrate with barium chloride, and evaporate to dryness. The residue contains sodium, potassium and lithium chlorides, and is digested with a mixture of absolute alcohol and ether, in which **lithium chloride** LiCl alone is soluble. This salt (m. pt. 606°) is one of the most deliquescent substances known, but **lithium fluoride** LiF is only sparingly soluble (cf. CaCl_2 and CaF_2).

Lithium burns with a white flame when heated in oxygen above its melting point, forming white **lithium monoxide** (*lithia*) Li_2O , which dissolves *slowly* in water with only moderate rise of temperature, producing **lithium hydroxide** LiOH . The latter is made by decomposing an aqueous solution of **lithium sulphate** Li_2SO_4 with baryta-water. It crystallises from solution as $\text{LiOH}\cdot\text{H}_2\text{O}$, and is a strong base. On heating the crystals in hydrogen below 140° a white porous mass of LiOH remains, and at 780° the oxide Li_2O is formed. **Lithium peroxide** Li_2O_2 is formed by drying over P_2O_5 the precipitate, $\text{Li}_2\text{O}_2\cdot\text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}$, obtained by adding hydrogen peroxide and alcohol to a solution of lithium hydroxide. Only a trace of lithium peroxide is formed when lithium burns in oxygen (cf. Na and K).

Lithium combines with nitrogen slowly at the ordinary temperature and rapidly on heating to form **lithium nitride** Li_3N (cf. magnesium). It is the only alkali metal to combine directly with nitrogen.

Lithium carbonate Li_2CO_3 , and **lithium phosphate** Li_3PO_4 , are sparingly soluble and are precipitated from lithium chloride solution by the corresponding sodium salts. The carbonate dissolves in a solution of carbon dioxide to form a solution of **lithium bicarbonate** LiHCO_3 , which is more soluble than the normal carbonate (cf. $\text{Ca}(\text{HCO}_3)_2$). The solution of the bicarbonate is called *lithia water*. On heating the normal carbonate in hydrogen at 780° it decomposes completely into the oxide and carbon dioxide (cf. CaCO_3). In these reactions lithium shows a much closer resemblance to the metals of the alkaline-earths, e.g. calcium, than to those of the alkalis. **Lithium nitrate** LiNO_3 is very deliquescent, and is soluble in alcohol. **Lithium sulphate** $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ is readily soluble in water and (unlike the sulphates of the other alkali-metals) is also soluble in alcohol.

Lithium salts, especially those of organic acids (citrate, salicylate) are used as a remedy for gout, since **lithium urate** is fairly soluble in water (1 part in 368 parts of H_2O at 20°).

Lithium salts give a crimson flame when moistened with hydrochloric acid and heated on a platinum wire in the Bunsen flame. The light emitted is resolved by the spectroscope into a very weak yellow line (6104 Å.) and :

brilliant crimson line (6708 Å.). Lithium is separated from potassium by the solubility of its chloroplatinate Li_2PtCl_6 , and from sodium by the solubility of its chloride in a mixture of absolute alcohol and ether and in pyridine, in which sodium chloride is insoluble.

Lithium hydride LiH is formed by direct combination of the elements. Fused LiH on electrolysis gives H_2 at the *anode*. Lithium forms the **sulphides** Li_2S , Li_2S_2 , and Li_2S_4 . The **carbide** Li_2C_2 is formed in the electric furnace, and with water evolves pure acetylene: $\text{Li}_2\text{C}_2 + 2\text{H}_2\text{O} = 2\text{LiOH} + \text{C}_2\text{H}_2$.

RUBIDIUM AND CAESIUM

Rubidium and caesium are rare. They occur in very small quantities in certain mineral waters (*e.g.* Dürkheim, Ungemach, Bourbonne-les-Bains—1 litre of the latter contains 18.7 mgm. of RbCl and 32.5 mgm. of CsCl). Rubidium salts are absorbed from the soil by plants, but caesium salts are not and act as vegetable poisons. These two elements were the first to be discovered by the spectroscope (Bunsen, 1860–61). They give reddish-lilac and blue flame colours, respectively (Latin *rubidus*—darkest red, and *caesius*—the blue colour of the sky). They also occur in lepidolite and some rare minerals. Carnallite contains about 0.035 per cent of RbCl , which collects in the mother liquor from the preparation of potassium chloride and is extracted from it. The richest source of caesium is the rare mineral *pollux* or *pollucite*, a hydrated caesium aluminosilicate found on the island of Elba.

These two elements may be separated from the other alkali-metals and from each other by the different solubilities of the chloroplatinates and of the alums: the amounts in gm. dissolved by 100 ml. of water at 20° are:

	K	Rb	Cs
Alums	13.5	2.27	0.619
M_2PtCl_6	1.12	0.141	0.070

Caesium may be separated as the characteristic *Godfrey's salt* $\text{Cs}_3\text{Sb}_2\text{Cl}_9$, precipitated by a solution of antimony trichloride in hydrochloric acid, which is decomposed by ammonia to give caesium chloride.

Caesium carbonate is soluble in alcohol, rubidium carbonate is practically insoluble.

Rubidium salts are widely distributed, although in small amounts, but caesium compounds are very rare. Although rubidium salts are absorbed by plants they cannot replace potassium, and the plants die unless the latter is provided. Rubidium is feebly radioactive, the isotope ^{87}Rb emitting β -rays.

Metallic caesium (first obtained by Setterberg in 1882) is best prepared by distilling the chloride with a large excess of calcium in vacuum in a nickel tube and condensing the vapour in a glass receiver; it is used in photoelectric cells, in which a very thin film of caesium is deposited on a very thin film of caesium oxide supported on silver. Both rubidium and (especially) caesium are very soft at room temperature and have a silver-white lustre.

The oxides of rubidium and caesium are:

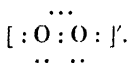
Rb_2O	Rb_2O_2	Rb_2O_3 (black)	RbO_2 (orange-yellow)
Cs_2O (orange-red)	Cs_2O_2	Cs_2O_3 (black)	CsO_2 (orange-red).

The dioxides MO_2 are formed by burning the metals in oxygen and the other oxides are obtained in succession by heating the dioxides in vacuum. Potassium dioxide KO_2 is the normal product of the combustion of potassium in oxygen. Sodium forms sodium peroxide Na_2O_2 , but by heating this in oxygen under high pressure at 450° the bright-orange sodium dioxide NaO_2 is formed.

The oxides M_2O_3 , M_2O_2 , and M_2O of rubidium and caesium are formed by heating the dioxides MO_2 in a vacuum. Sodium sesquioxide Na_2O_3 is formed as a rose-red precipitate by passing oxygen into a solution of sodium in anhydrous liquid ammonia.

The peroxides M_2O_2 of all the alkali metals contain the ion $[\text{:}\overset{\cdot\cdot}{\text{O}}\text{:}\overset{\cdot\cdot}{\text{O}}\text{:}]'$;

the dioxides MO_2 contain the paramagnetic superoxide ion with one odd electron and may be represented with a three-electron bond (p. 437)

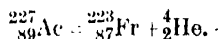


Potassium trioxide KO_3 is obtained in red-brown needles by the action of ozone on dry powdered potassium hydroxide and extracting with liquid anhydrous ammonia. It reacts violently with water, evolving oxygen and forming potassium hydroxide. It is paramagnetic and contains the

linear ion $[\text{:}\overset{\cdot\cdot}{\text{O}}\text{:}\overset{\cdot\cdot}{\text{O}}\text{:}\overset{\cdot\cdot}{\text{O}}\text{:}]'$, with the three-electron bond resonating.

FRANCIUM

The radioactive element **francium** is formed as a branch-change product by α -ray emission from actinium:



It behaves chemically as an alkali metal.

CHAPTER XXXVII

COPPER, SILVER, AND GOLD

THE metals of the odd series (or sub-group *b* elements) of Group I occur in Nature in the free state or else are very easily formed by the reduction of their compounds, so that they were the earliest known elements. Although they occur in the same group as the alkali-metals, the sole similarity is the existence of a series of compounds MX , in which the metals are univalent. Some compounds of bivalent silver are known. Copper forms compounds in which it is bivalent CuX_2 , and gold a series in which it is trivalent AuX_3 , and both these are better known than the univalent series. Unlike the alkali-metals, copper, silver and gold readily form *complex compounds*, in which the metal may be present either in the positive radical, e.g. $[Cu(NH_3)_4]SO_4$, or in the negative radical, e.g. $K[Ag(CN)_2]$.

	Copper	Silver	Gold
Atomic number -	29	47	79
Electron configuration	2·8·18·1	2·8·18·18·1	2·8·18·32·18·1
Density - - -	8·94	10·47	19·5
Atomic volume - - -	7·12	10·3	10·2
Melting point - - -	1083·0°	960·5°	1063·0°
Boiling point - - -	2310°	1955°	2610°
Colour of vapour - -	green	blue	—

Copper, silver, and gold are *transitional elements* in the wider sense (p. 370). Gold, with the highest atomic weight, differs from the other members of the group, and this type of anomaly occurs elsewhere in the periodic table. Gold in many ways resembles platinum. Copper also shows a much closer relationship with mercury than with silver or gold, although the cuprous salts resemble those of silver. Cuprous and silver chlorides are both white and insoluble but dissolve readily in ammonia. Although silver chloride is quite stable, cuprous chloride is readily oxidised to the cupric compound. The sulphides of copper and silver are isomorphous; the mineral *copper glance*, consisting chiefly of cuprous sulphide Cu_2S , contains silver sulphide Ag_2S in varying amounts.

When copper, silver and gold function with higher valencies (2 and 3), electrons must be brought out from the inner group of 18, which is then left as an incomplete group (17 or 16). The *bivalent* copper and silver ions contain an odd electron and the salts are coloured and paramagnetic. The *trivalent* gold compounds are probably always covalent, and it is doubtful if bivalent gold exists.

Silver oxide is a much stronger base than cuprous or aurous oxides, being comparable with cupric oxide, and the cuprous oxy-salts (carbon-

ate, nitrate and sulphate) are much less stable than the silver salts. Cupric and silver carbonates are easily decomposed by heat, Ag_2CO_3 at 200° . The cuprous salts are easily oxidised to cupric salts, whilst argentic salts are formed only by powerful oxidising agents, and are usually stable only in coordination compounds, e.g. with pyridine.

Tervalent gold shows analogies with trivalent aluminium, indium and thallium; the hydroxide $\text{Au}(\text{OH})_3$ is, like aluminium hydroxide, amphoteric and soluble in acids and in alkalis.

COPPER

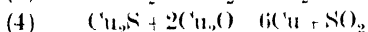
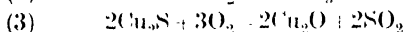
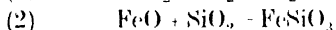
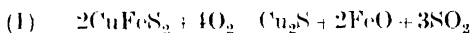
History.—Copper ores are easily reduced and the metal was used in very early times, the oldest specimens of cast copper from Egypt and Babylonia dating to about 4000 B.C. It appeared later in the form of its alloy bronze, which contains copper and tin. Working in bronze was practised by the Sumerians at Ur in 3500 B.C. and in Egypt at least as early as 2500 B.C.

Copper was obtained by the Greeks and Romans from the island of Cyprus; the Latin name *aes cyprium* or Cyprian copper afterwards became simply *cyprium*, and finally *cuprum*. These names were (with the Greek *chalkos*) also used for brass and bronze. The alchemists associated the metal with the planet Venus and designated it by the symbol ♀. The precipitation of copper from the drainage-water of copper mines by iron was considered to be a case of transmutation, until Van Helmont pointed out that the liquid originally contained a salt of copper derived from copper pyrites in the mine. Boyle (1675) explained the reaction as one of simple displacement.

Occurrence.—*Native copper* occurs in Sweden, the Ural mountains, and in large quantities in America, near Lake Superior. It usually contains small quantities of silver, also bismuth and lead. Cuprous oxide Cu_2O occurs as *cuprite* (or *red copper ore*), cupric oxide CuO in smaller amounts as *tenorite* or *melanconite*. Compounds of the carbonate and hydroxide occurring native are the bright-green *malachite* $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, and deep-blue *azurite* (or *chessylite*) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, which are used in works of art. In combination with sulphur alone copper occurs in small amounts as *chalcocite* or *copper glance* Cu_2S and *covellite* or *indigo copper* CuS , both probably formed by reduction of the sulphate by organic matter. The commonest ores of copper are *copper pyrites* or *chalcopyrite* CuFeS_2 and *bornite* (*erubescite* or *variegated copper ore*) Cu_3FeS_3 , i.e. sulphides of copper and iron. Copper is extracted by the "wet process" from burnt cuprous pyrites used in making sulphuric acid (p. 476), and also from drainage water from stocks of such pyrites. Large quantities of copper now come from the Katanga region of the Belgian Congo and from Roan Antelope in N. Rhodesia, the ores being mostly malachite and *chrysocolla* $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$. The basic chloride *atacamite* $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ is important in Chile and Peru.

Copper occurs in the red colouring matter (*turacin*) of the feathers of the plantain-eater (*Touracus*), and in the *haemocyanin* of the blood of the cuttlefish, which acts like haemoglobin as an oxygen carrier but is blue in arterial and colourless in venous blood. Minute quantities of copper occur in plants, especially in green peas. Ordinary bread contains 4 mgm. of Cu per kg., potatoes 2 mgm. Although the daily consumption of copper in food is about 1 mgm., it is said that up to 100 mgm. may be taken per day without danger, and higher organisms appear to have become to some extent immune to copper, although traces of lead and mercury are poisonous to them. Copper seems to be necessary to assist in the mobilisation of iron in the body and in the formation of haemoglobin. Milk has a low copper content. Lower organisms are very sensitive to copper salts and traces are added to drinking water in America to destroy bacilli and algae. A solution of copper sulphate mixed with slaked lime is used as *Bordeaux mixture* as a fungicide. Seed corn may be steeped in 0.5 per cent copper sulphate solution to prevent the development of "smut".

Metallurgy of copper. - Native copper is melted with a flux and refined. Oxides (*e.g.* cuprite) and carbonates (*e.g.* malachite) are reduced by heating with carbon. Sulphide ores, *e.g.* copper pyrites CuFeS_2 , from which a large amount of copper is obtained, are smelted by a somewhat complicated process. The separation of the iron and sulphur from the copper in the ore is difficult, since sulphur has a greater affinity for copper than for iron. The essential part of the process is to get rid of the iron by oxidation as ferrous silicate in the slag and leave the copper as cuprous sulphide. This on roasting in air is partly converted into cuprous oxide, which reacts with the remaining sulphide to form metallic copper :



The ore is first roasted in a large flat furnace, being raked on the hearth to expose a large surface to the air. Part of the copper and iron are oxidised and arsenic is volatilised as oxide. The roasted ore is then heated in a reverberatory furnace (Fig. 361) with silica. In the furnace the flames are deflected from the roof on to the charge on the hearth. A fusible ferrous silicate slag is formed together with a lower layer of *matte* or *coarse metal*, containing ferrous and cuprous sulphides. On repeating the process nearly pure cuprous sulphide, called *white* or *fine metal*, is obtained.

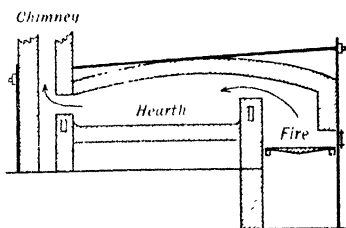


FIG. 361. Reverberatory furnace.

In the original "Welsh process", the blocks of fine metal were roasted in a current of air on the hearth of a reverberatory furnace, when reactions (3) and (4) occurred. In modern practice the molten white

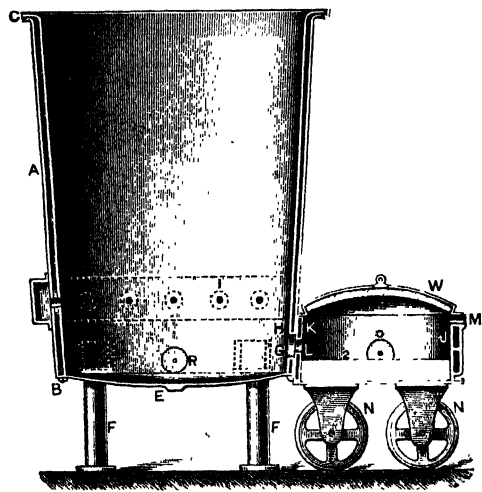


FIG. 362.- Lower part of blast furnace for copper.

metal is charged into a Bessemer converter and a blast of air sent through it (Fig. 362). Reactions (3) and (4) occur.

It is essential to the success of this process, as was shown by the French metallurgist Manhès in 1880, that the air blast shall be admitted through ports I in an annular pipe above the base of the converter, so that the metal formed drops below and is removed from the oxidising action of the blast; in steel-making, on the other hand, the blast is sent through the base of the converter.

Attempts have been made to smelt sulphide ores directly in a blast furnace, using the sulphur in the ore to supply most of the heat, but this method is not suitable for powdered ore and in America (*e.g.* at Anaconda) very large reverberatory furnaces with sand hearths and fired by gas, oil or powdered coal are used.

In copper extraction by *wet processes*, burnt pyrites are roasted with common salt to form cupric chloride which is dissolved in water. Any silver and gold present are precipitated as iodides by adding sodium iodide, and the copper is then precipitated by scrap iron. Spanish Rio Tinto pyrites are stacked in immense heaps exposed to air and rain, when copper sulphate solution is formed and drains out; the copper is precipitated by scrap iron and the pyrites exported for sulphuric acid manufacture.

Copper refining.—The crude copper obtained by smelting is usually full of bubbles caused by the escape of gas in reaction (4), and is called *blister copper*. It may contain over 98 per cent of copper but requires refining, for two reasons: (1) copper is used in making wires or cables for carrying electric current and the conductivity is appreciably lowered by traces of impurities; (2) the crude copper may contain traces of silver and gold, which pay for extraction.

The copper is often given a preliminary purification by melting on a furnace hearth, when atmospheric oxygen dissolves in the metal and

oxidises impurities such as iron, which form a slag with silica. The small amount of cuprous oxide formed is removed by "poling", in which a pole of green wood is thrust into the melted metal. Torrents of reducing gas (containing methane) bubble up through the metal and reduce the oxide.

The blocks of copper are then finally purified by an electrolytic process. They are made the anodes in a bath of copper sulphate solution acidified with sulphuric acid. The cathodes are thin sheets of pure copper (Fig. 363). The copper dissolves from the anode as cupric ions

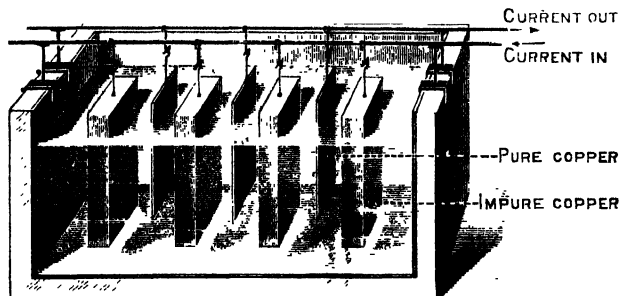


FIG. 363.—Purification of copper by electrolysis (diagrammatic).

Cu^{++} , which travel to the cathode, where they give up their charges and are deposited as pure copper. Iron, nickel, cobalt, arsenic and zinc pass into solution; gold, silver and any platinum metals (with some impurities, e.g. selenium, tellurium and lead) fall as an *anode slime*, which is collected for the purpose of obtaining the precious metals. The electrolytic copper is 99.96–99.99 per cent pure.

A similar process (Jacobi, 1837) is **electrotyping**, used in reproducing statues and other works of art. The copper may be deposited on plaster casts covered with graphite to render them conducting, and the shell stripped off. In the same way, if an impression of printers' type is taken on plastic material and the latter covered with powdered graphite, a thin deposit of copper may be formed over the surface by electrolysis. This is stripped off and backed by pouring on molten type metal. The plate may then be used for printing.

Copper may be deposited on iron by dipping the metal in a solution of copper cyanide in potassium cyanide, when a thin *adherent* film of copper is deposited (a spongy deposit is produced from copper sulphate); this is then thickened by electrolysis in a solution of copper sulphate. Iron rollers are in this way covered with copper for use in calico-printing.

Copper is used for the driving-bands of steel projectiles. The driving-band consists of a copper band recessed into a groove in the base of the shell, and projecting slightly above the surface of the latter so as to be somewhat larger than the bore of the gun. On firing the shell, the copper is squeezed into the spiral rifling of the gun-barrel, and the gases are prevented from escaping, whilst the shell acquires a rotation which serves to keep it in its trajectory without turning over.

Alloys of copper.—The alloys of copper with other metals are of technical importance. *Brass*, *Dutch metal*, *Muntz metal*, and *Delta metal* (copper + zinc), and *bronze*, *speculum metal* and *bell metal* (copper + tin), are made by fusing the copper, and adding the requisite amount of zinc or tin. *Coinage metal* contains copper, tin and zinc.

	Copper.	Tin	Zinc	Iron
Brass - - -	4	—	1	—
Bronze (gun-metal)	9	1	—	—
Speculum metal -	2	1	—	—
Bell metal - -	4-5	1	—	—
Delta metal - -	55	—	41	4 Fe etc.
Dutch metal - -	80	—	20	—
Muntz metal - -	60	—	40	—
Old Roman coin -	96.06	—	2.71	0.85
Modern bronze coin	95	1	1	—
Phosphor bronze -	94.75 82.5	5-15	phosphorus	0.25-2.5

Casting bronze usually contains some zinc and lead. Bronze for machinery is 80-90 copper, 5-18 tin and 2-10 zinc. The best *brass* is 4 copper and 1 zinc; common brass contains 22-30 per cent of zinc, but metal with 35-40 per cent zinc can still be worked. *Silicon bronze* is used for telegraph wires. *Phosphor bronze* is hard, elastic, and tough. *delta metal* can be forged and rolled as well as cast, and is used for bearings, valves, and ships' propellers. *Muntz metal* is used as a sheathing for wooden ships. *Monel metal* is 7 copper + 3 nickel.

Properties of copper.—A new surface of pure copper appears salmon-pink in colour, but the colour produced by selective reflexion is a deep rose-red, as is seen by looking at the fold of a piece of copper foil cleaned with nitric acid and bent to a V-shape. The light is then reflected many times from the surface of the metal before entering the eye. The complementary colour green is seen in the light transmitted through thin leaves of the metal, and fused copper also emits a green light at high temperatures.

Pure copper is very malleable and ductile and can be rolled into sheets, hammered into thin leaves, and drawn into wire. The metal may also be "spun" on the lathe in the production of seamless vessels. Just below the melting point copper becomes brittle, and small quantities of impurities reduce the malleability of the metal.

Pure copper powder is produced by dissolving zinc in a slightly acidified solution of copper sulphate, washing the precipitated copper with hot water and alcohol, and removing the small quantity of occluded hydrogen by heating in a vacuum.

Copper combines directly with chlorine, bromine, iodine, oxygen and sulphur.

In pure dry air copper remains bright, but in town air it rapidly tarnishes, becoming covered with a very thin adherent brown film. On prolonged exposure a green film of basic sulphate (see p. 730) is formed. On heating in air the metal is readily oxidised and the product forms scales which are black on the outside (cupric oxide CuO), but red on the side in contact with the metal (cuprous oxide Cu_2O). If heated for a long time in air cupric oxide is formed. When heated in the oxygen-hydrogen blowpipe the metal burns with a very brilliant green flame. Copper does not decompose water at the ordinary temperature, or steam at a red heat.

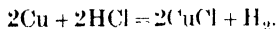
Copper is not acted upon by dilute sulphuric or hydrochloric acid in absence of oxygen; hot concentrated sulphuric acid converts it into the sulphate. The metal readily dissolves in dilute nitric acid (unless this is quite free from nitrous acid) with evolution of nitric oxide; it dissolves slowly, *with evolution of hydrogen*, in hot concentrated hydrochloric acid, and more rapidly in hot concentrated hydrobromic and hydriodic acids, cuprous compounds being formed.

Copper forms two series of compounds, the cupric compounds CuX_2 in which it is bivalent, and the cuprous compounds CuX in which it is univalent.

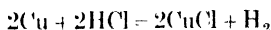
CUPROUS COMPOUNDS

Cuprous hydride CuH is obtained as an unstable brownish-yellow precipitate by reducing a solution of copper sulphate, acidified with a little sulphuric acid, with sodium hypophosphite at 70° : $2\text{CuSO}_4 + 3\text{H}_3\text{PO}_2 + 3\text{H}_2\text{O} = 2\text{CuH} + 3\text{H}_3\text{PO}_3 + 2\text{H}_2\text{SO}_4$. It evolves hydrogen with concentrated hydrochloric acid: $\text{CuH} + \text{HCl} = \text{CuCl} + \text{H}_2$.

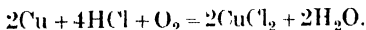
Cuprous chloride CuCl is formed as a brown mass when copper burns in a limited supply of chlorine, or hydrogen chloride is passed over heated copper:



Copper dissolves slowly in hot concentrated hydrochloric acid:



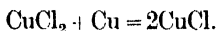
It dissolves more easily in presence of oxygen, when cupric chloride is first formed, but is reduced to cuprous chloride by the copper:



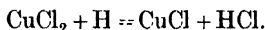
Cuprous chloride is most easily prepared by dissolving cuprous oxide in concentrated hydrochloric acid, or by reducing a solution of cupric chloride.

The cupric chloride may be reduced: (a) By boiling with concentrated hydrochloric acid and copper turnings until the solution becomes

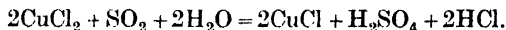
colourless. On pouring into water, white cuprous chloride is precipitated :



(b) By treating with zinc-dust and hydrochloric acid :



(c) By passing sulphur dioxide into the solution :



A mixture of cupric sulphate and sodium chloride may be used in the last case instead of cupric chloride.

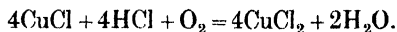
The following are convenient methods for the preparation of cuprous chloride :

A. Dissolve 25 gm. of cupric oxide in 250 ml. of concentrated hydrochloric acid in a flask. Add 50 gm. of copper turnings and boil in a fume-cupboard until the solution is colourless. Pour into a litre of previously boiled distilled water, filter off the cuprous chloride in a Buchner funnel, and wash rapidly in succession with a dilute solution of sulphurous acid, alcohol, and ether. Dry on a porous plate in a vacuum desiccator over sulphuric acid.

B. Pass sulphur dioxide into a solution of 25 gm. of crystallised copper sulphate and 12 gm. of common salt in 70 ml. of water till the liquid, even on standing, smells strongly of the gas. Cuprous chloride slowly crystallises out and a further quantity separates after boiling ; it is filtered and treated as in A.

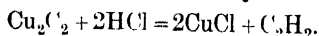
Cuprous chloride is a white powder which crystallises from concentrated hydrochloric acid in white tetrahedra. It melts at 422° , forming a brown resinous mass on cooling ; the boiling point is 1366° and the vapour density corresponds with Cu_2Cl_2 . If exposed to light when moist it becomes dark-coloured (*cf.* AgCl), and in moist air it forms green basic *cupric* chloride $\text{CuCl}_2 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$.

Cuprous chloride is insoluble in water but dissolves in *concentrated* hydrochloric acid to form a solution which is colourless when every trace of oxygen is excluded, *e.g.* by keeping in a closed bottle over bright copper turnings. The solution in hydrochloric acid probably contains the complex acid H_2CuCl_3 or the ion CuCl_3'' (containing 1-valent copper) ; it rapidly becomes green or yellow on exposure to air owing to oxidation and formation of cupric chloride :



The solution in hydrochloric acid is used in gas analysis for the absorption of carbon monoxide, when a compound $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ is formed. Cuprous chloride dissolves readily in ammonia, forming a colourless solution of $\text{Cu}(\text{NH}_3)\text{Cl} \cdot \text{H}_2\text{O}$ if all traces of oxygen are excluded, as by standing over bright copper turnings in a closed bottle. Crystals of this compound are obtained by boiling copper powder with a solution

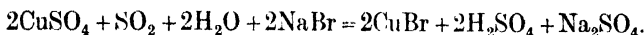
of ammonium chloride, and cooling. The solution of cuprous chloride in ammonia becomes deep blue when exposed to air, $\text{Cu}(\text{NH}_3)_4\text{Cl}_2$ (containing 2-valent copper) being formed. The ammoniacal solution of cuprous chloride is used in gas analysis to absorb carbon monoxide and acetylene; with acetylene it forms a bright red precipitate of cuprous acetylide Cu_2C_2 . This is explosive when dry; when warmed with concentrated hydrochloric acid it evolves acetylene:



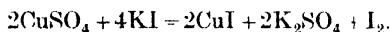
Dry cuprous chloride absorbs ammonia gas to form compounds of CuCl with 3, $1\frac{1}{2}$, and 1NH_3 .

Cuprous chloride is soluble in sodium thiosulphate solution, and slightly soluble in potassium hydroxide solution.

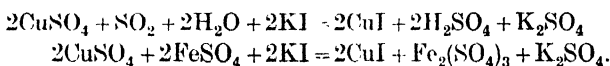
Cuprous bromide CuBr is formed with incandescence as a brown solid when bromine acts upon heated copper, but is most conveniently prepared as a white precipitate by passing sulphur dioxide into a solution of 20 gm. of copper sulphate crystals and 8 gm. of sodium bromide in 300 ml. of water:



Cuprous iodide CuI is formed by heating copper in iodine vapour and is precipitated as a very insoluble white powder on addition of potassium iodide to a solution of cupric sulphate. Cupric iodide first produced as a green precipitate is unstable and decomposes into cuprous iodide and free iodine:



If sulphur dioxide or ferrous sulphate is previously added, the iodine is reduced and forms cuprous iodide:



Dissolve 10 gm. of blue vitriol and 12.5 gm. of green vitriol in 250 ml. of water and add 7.0 gm. of KI in 75 ml. of water. Filter, wash, and dry the 7.5 gm. of CuI produced.

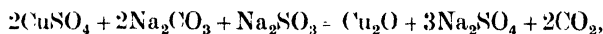
The formation of iodine in the first reaction is applied in the volumetric determination of copper.

Excess of potassium iodide solution is added, and not more than 3 ml. of concentrated HCl or H_2SO_4 or (best) 25 ml. of 50 per cent acetic acid for 100 ml. of solution. Starch is added when the yellow colour of the iodine is nearly discharged by thiosulphate and titration is continued till the colour is discharged. "After blueing" may occur on standing but is prevented by adding KCNS at the end of the titration. The solution should contain about 0.1 gm. of copper in the volume titrated and 5 times as much KI as copper is added.

Cuprous iodide becomes red and then black on heating, but becomes white on cooling. It is sparingly soluble in alkali iodide solution but

readily soluble in ammonia and in solutions of potassium cyanide and sodium thiosulphate.

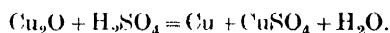
Cuprous oxide Cu_2O is a red solid formed by strongly heating cupric oxide with copper filings, or by the partial reduction of cupric compounds in the presence of alkalis, *e.g.* by boiling a solution containing cupric sulphate, sodium carbonate and sodium sulphite :



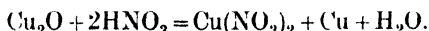
or by boiling a solution (Fehling's solution) containing cupric sulphate, Rochelle salt and sodium hydroxide, with grape sugar.

Dissolve 6.9 gm. of pure copper sulphate crystals in 100 ml. of water, adding 1 drop of sulphuric acid. Call this *Solution A*. Dissolve in 100 ml. of water 35 gm. of Rochelle salt (sodium potassium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and 10 gm. of sodium hydroxide. Call this *Solution B*. Mix together 25 ml. of *A* and 25 ml. of *B*: the resulting deep-blue liquid is called **Fehling's solution**. Boil this in a porcelain dish with a solution of glucose (grape sugar). A yellow precipitate is deposited, which quickly turns to bright-red cuprous oxide Cu_2O . Filter, wash with boiling water and alcohol, and dry in a steam oven.

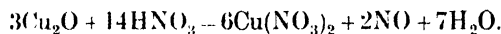
Cuprous oxide gives a red colour to the borax bead. When fused with glass it forms the cheaper kind of *ruby glass*. With dilute sulphuric acid it gives a solution of *cupric* sulphate and metallic copper separates :



Dilute nitric acid in the cold reacts with cuprous oxide to form a solution of *cupric* nitrate and copper :

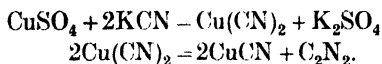


With more concentrated nitric acid, or with dilute acid on heating, cuprous oxide dissolves with evolution of nitric oxide :



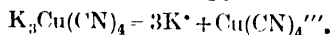
Concentrated hydrochloric acid dissolves cuprous oxide with formation of a colourless solution of *cuprous* chloride CuCl or a complex acid H_2CuCl_3 . Cuprous oxide dissolves in concentrated ammonia to form a colourless solution if oxygen is excluded, otherwise a blue solution containing a cupric compound is formed.

Cuprous cyanide CuCN is the only stable cyanide of copper. When potassium cyanide solution is added to a solution of cupric sulphate, the yellow cupric cyanide first precipitated rapidly decomposes with evolution of cyanogen gas and white cuprous cyanide is formed :

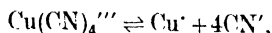


This dissolves in a solution of potassium cyanide, forming a colourless

solution of potassium cuprocyanide $K_3Cu(CN)_4$, which is a salt of a complex anion containing univalent copper :

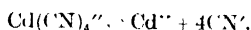


Only traces of copper ions are formed from the further ionisation :

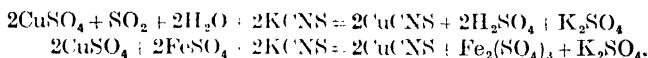


and the solution is not precipitated by hydrogen sulphide, since the concentration of copper ions is not sufficient to exceed the solubility product of the very sparingly soluble cuprous sulphide.

If cadmium is present, a complex cadmiocyanide (p. 315) is formed, but the ion $Cd(CN)_4''$ is sufficiently ionised to give enough cadmium ions to exceed the solubility product of cadmium sulphide :



Potassium thiocyanate gives with a solution of cupric sulphate to which sulphur dioxide or ferrous sulphate has been added a white precipitate of cuprous thiocyanate $Cu^{\cdot}CNS$ insoluble in hydrochloric acid :

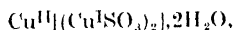


Cuprous sulphide Cu_2S , the stable sulphide of copper (p. 731), is formed as a blue-black brittle mass when sulphur and copper turnings are heated in a small flask, the copper burning in the sulphur vapour. The *pure* compound is obtained only when the reaction is carried out in a vacuum at a high temperature. Cuprous sulphide is formed by heating cupric sulphide in a current of hydrogen or carbon dioxide, and it is precipitated by hydrogen sulphide from a solution of cuprous chloride in hydrochloric acid :

$$2CuCl + H_2S = Cu_2S + 2HCl.$$

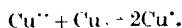
Cuprous sulphide is only slowly decomposed by chlorine at a red heat and is scarcely attacked by fused sodium carbonate. When fused with alkali sulphides it forms steel-blue insoluble thiocuprites, *e.g.* $KCuS$ and $Na_2Cu_4S_3$.

Cuprous sulphite is present in the red crystalline *Chevreul's salt*

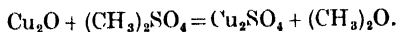


precipitated by passing sulphur dioxide into a solution of cupric acetate in acetic acid, and boiling.

Cuprous sulphate Cu_2SO_4 is formed to some extent when cupric sulphate solution stands in contact with copper :



This is the cause of the inaccuracy of the ordinary copper coulometer. The pure salt is obtained as a white powder by heating cuprous oxide with dimethyl sulphate, washing with ether and drying *in vacuo* :



It is at once decomposed by water, with deposition of copper : $\text{Cu}_2\text{SO}_4 - \text{CuSO}_4 + \text{Cu}$. Its compound with ammonia $\text{Cu}_2\text{SO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ is more stable.

CUPRIC COMPOUNDS

Cupric chloride CuCl_2 is obtained anhydrous as a dark-brown mass by burning copper in excess of chlorine or by heating the hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in hydrogen chloride gas at 150° . It is formed as a yellow powder by adding concentrated sulphuric acid slowly to a concentrated solution of cupric chloride. When strongly heated it loses chlorine and leaves cuprous chloride. A crystalline hydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is formed in emerald-green crystals by dissolving cupric oxide in concentrated hydrochloric acid and evaporating. When free from moisture the crystals are blue.

In concentrated solutions cupric chloride is yellowish-green and on adding concentrated hydrochloric acid the colour becomes yellow. This may be due to the reversal of the ionisation : $\text{CuCl}_2 \rightleftharpoons \text{Cu}^{++} + 2\text{Cl}^-$, the colour of the undissociated salt being yellow, or perhaps a complex acid H_2CuCl_4 is formed. A very dilute solution shows the pure blue colour of the hydrated cupric ion ; the green solutions probably contain a mixture of the blue ion and the yellow un-ionised form or complex acid. Cupric chloride is very deliquescent and is also soluble in alcohol. The alcoholic solution burns with a fine green flame.

On cooling a concentrated solution of cupric chloride which has been saturated with hydrogen chloride, dark red needles of one of the complex acids $\text{HCuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{CuCl}_4 \cdot 5\text{H}_2\text{O}$, and $\text{H}_3(\text{CuCl}_5)$ are formed, salts of which are known. The compound $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ crystallises on cooling a hot solution of cupric chloride saturated with ammonia gas. Compounds of dry CuCl_2 with 6, 4, $\frac{1}{3}$, and 2NH_3 are known.

Basic cupric chloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ is formed as a pale-blue precipitate when potassium hydroxide is added to excess of cupric chloride solution. It occurs in Atacama, Peru, Bolivia, etc., in the form of a crystalline green sand called *atacamite*, and is being formed by the action of sea water on copper pyrites on the south coast of Chile and in Adelaide, Australia. The basic chloride is prepared for use as a pigment called *Brunswick green* by boiling copper sulphate solution with a small quantity of bleaching powder.

Cupric fluoride CuF_2 is a white powder formed by the action of fluorine on copper powder, or by heating the blue hydrate $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ (from a solution of CuO in hydrofluoric acid) in a current of HF below 500° .

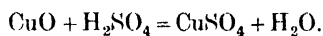
Cupric bromide CuBr_2 is formed in black crystals by evaporating a solution of the oxide in hydrobromic acid in a vacuum desiccator over quicklime. In solution, it shows the same colour changes as the chloride. The green crystal hydrate $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ is not easily obtained.

The crystalline complex acid $\text{HCuBr}_3 \cdot 2\text{H}_2\text{O}$ and corresponding salts are known.

Cupric iodide CuI_2 is unstable and quickly decomposes into cuprous iodide and iodine, but in combination with ammonia and ethylenediamine it is stable in the form of the compounds $\text{CuI}_2 \cdot 4\text{NH}_3$ and $\text{Cu}(\text{en})_2\text{I}_2 \cdot 1$ or $2\text{H}_2\text{O}$. Cupric nitrite, cyanide and sulphate behave similarly. The black **cupric thiocyanate** $\text{Cu}(\text{CNS})_2$, can be prepared as a solid.

Cupric oxide or *black oxide of copper* CuO is formed by prolonged heating of the metal (e.g. pieces of wire or turnings) in air or oxygen, or by heating cupric nitrate: $2\text{Cu}(\text{NO}_3)_2 \rightarrow 2\text{CuO} + 4\text{NO}_2 + \text{O}_2$. A purer oxide is formed by heating the basic carbonate. Cupric oxide is a black solid which is stable up to about 800° but at higher temperatures it evolves oxygen and forms some cuprous oxide Cu_2O . Hot cupric oxide is readily reduced to metal by hydrogen, carbon or organic substances. The oxide dissolves in a borax bead, colouring it blue. If a little tin oxide or stannous chloride is added, the cupric oxide is reduced to cuprous oxide which forms an opaque red bead. Cupric oxide is used to give blue and green colours to glass.

When cupric oxide is dissolved in dilute acids, blue solutions of cupric salts are formed, e.g. :



Concentrated hydrochloric acid gives a yellow solution of cupric chloride CuCl_2 .

On adding a solution of potassium or sodium hydroxide to a solution of a cupric salt, a pale-blue gelatinous precipitate of **cupric hydroxide** is formed, insoluble in excess of alkali but soluble in ammonia. With excess of cupric salt, the precipitate (as stated by Berthollet) is a basic salt $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, or $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$. If a little of copper salt solution is added to an excess of concentrated alkali, a deep-blue colloidal solution is formed. A crystalline hydroxide, $\text{Cu}(\text{OH})_2$, is obtained by adding ammonia to a boiling solution of copper sulphate till the green precipitate becomes blue, washing, and warming with fairly concentrated sodium hydroxide solution.

If the pale-blue precipitated hydroxide is boiled with water it forms a black solid usually formulated as $4\text{CuO} \cdot \text{H}_2\text{O}$ which is granular and easily filtered. On heating to dull redness this forms CuO .

Cupric hydroxide readily dissolves in ammonia, forming a deep-blue solution known as *Schweizer's reagent*. This dissolves cellulose (filter paper, cotton wool), and if the solution is squirted into dilute acid a thread of amorphous cellulose is formed which is one variety of artificial silk. The solution may also be applied to canvas to form a water-tight coating of amorphous cellulose (*Willesden canvas*). The blue ammoniacal solution contains $\text{Cu}(\text{OH})_2(\text{NH}_3)_2$ and $\text{Cu}(\text{OH})_2(\text{NH}_3)_4$.

A red copper sesquioxide Cu_2O_3 , probably containing trivalent copper, is formed by the action of potassium persulphate on a suspension of cupric hydroxide in baryta water, or by electrolytic oxidation of copper in very concentrated sodium hydroxide, and it appears to form **percuprates**, e.g. BaCu_2O_4 . Hydrogen peroxide converts cupric hydroxide, or a solution of cupric hydroxide in potassium hydroxide, or sodium cupric carbonate, into yellowish-brown hydrated **copper peroxide**, possibly $(\text{HO})\text{Cu}-\text{O}-\text{O}-\text{Cu}(\text{OH})$, which forms hydrogen peroxide with acids.

Only **basic cupric carbonates** are known; the most important are the minerals *chessylite* (or *azurite*) $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (deep blue) and *malachite* $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (bright green). On heating, basic copper carbonates lose water and carbon dioxide and leave black cupric oxide.

The green patina formed on copper exposed to air, usually described as the basic carbonate, is nearly always the basic sulphate $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, which occurs as the mineral *brochantite*, although occasionally the basic carbonate is present. In places near the sea or where salt spray is carried by the wind the basic chloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ (*atacamite*) is formed. The definite compounds are formed only after a prolonged exposure of about 70 years.

The pale blue precipitate formed on adding sodium carbonate solution to copper sulphate solution has the composition of azurite.

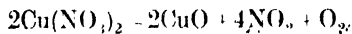
The X-ray spectra show that the structures of azurite and malachite are $\text{Cu}_2(\text{OH})_2(\text{CO}_3)_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$. Blue crystals of **sodium cupric carbonate** $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ are formed by warming the precipitated basic carbonate with a solution of sodium carbonate and bicarbonate. Cupric carbonate forms stable coordination compounds with ammonia and ethylenediamine, $\text{Cu}(\text{NH}_3)_2\text{CO}_3$ and $\text{Cu}(\text{en})_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$.

A mixture of basic carbonates called *verditer* is precipitated by a solution of sodium carbonate from a solution of a cupric salt. Azurite dissolves in a hot solution of sodium bicarbonate and on boiling the solution deposits a green powder of malachite.

Cupric acetate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ forms dark-green crystals; the **basic acetate** $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Cu}(\text{OH})_2$ is the bright-green pigment *verdigris*, made by allowing plates of copper to stand with alternate layers of "mares" (grape skins after pressing the juice from the grapes in wine factories), then packing the sheets on end and moistening with sour wine, which forms acetic acid (CH_3COOH) :



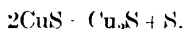
Cupric nitrate is prepared by dissolving the metal, oxide, or basic carbonate in dilute nitric acid, and on evaporation forms blue deliquescent prismatic crystals of $\text{Cu}(\text{NO}_3)_2 \cdot 3$ (or 6) H_2O . On heating, they lose water and nitric acid, forming a basic salt $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ which is also precipitated from solution by ammonia. Cupric nitrate decomposes on heating:



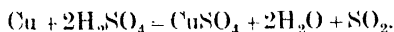
It has powerful oxidising properties : if a few crystals are moistened and wrapped in tinfoil, sparks are emitted. The anhydrous salt is obtained as a white powder by the action of a solution of nitrogen pentoxide in fuming nitric acid on the crystalline hydrate.

Cupric nitrite is known only in complex and coordination compounds such as $K_3Cu(NO_2)_6$ and $Cu(NH_3)_4(NO_2)_2 \cdot 2H_2O$.

Cupric sulphide CuS is a black solid formed by heating copper powder with excess of flowers of sulphur at a temperature below 440° , by the action of a solution of sulphur in carbon disulphide on copper powder, or by precipitating an acid solution of a cupric salt with hydrogen sulphide. (The precipitate usually contains cuprous sulphide and sulphur.) In the moist state it is rapidly oxidised by air, forming a blue solution of the sulphate. It is slightly soluble in yellow ammonium sulphide and the hot solution on cooling deposits crystals of $(NH_4)CuS_4$; similar compounds are formed with other alkali metals, and they may contain cuprous copper, *i.e.* are salts of $HCu^+S_4^-$, derived from H_2S_4 . Cupric sulphide is less stable than cuprous sulphide and loses sulphur when gently heated alone or in hydrogen :

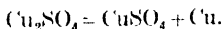


Cupric sulphate $CuSO_4$, generally known simply as *copper sulphate*, the commonest cupric salt, crystallises from water in large blue triclinic crystals $CuSO_4 \cdot 5H_2O$ called *blue vitriol* or *bluestone*. It is obtained by dissolving cupric oxide or basic carbonate in dilute sulphuric acid and crystallising. Anhydrous cupric sulphate is formed in the preparation of sulphur dioxide by heating copper with concentrated sulphuric acid :



Crystallised copper sulphate is obtained from the cold residue by dissolving in water, filtering and evaporating. Some black copper sulphide is also formed.

According to Cundall (1914) the reaction first forms cuprous sulphate Cu_2SO_4 ; if the acid liquid is cooled, filtered through asbestos, and poured into water, a red precipitate of copper is formed :



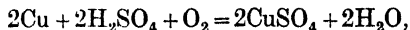
Cuprous sulphide Cu_2S deposits as a black powder in the earlier stages of the reaction, *but is afterwards mostly decomposed* and the final product is almost entirely $CuSO_4$:

1. $8Cu + 4H_2SO_4 = 3Cu_2SO_4 + Cu_2S + 4H_2O.$
2. $2Cu + 2H_2SO_4 = Cu_2SO_4 + 2H_2O + SO_2.$
3. $5Cu_2SO_4 + 4H_2SO_4 = Cu_2S + 8CuSO_4 + 4H_2O.$
4. $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + 2H_2O + SO_2.$
5. $CuS + 4H_2SO_4 = CuSO_4 + 4SO_2 + 4H_2O.$

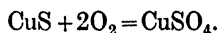
Equations (1) and (3) give Pickering's equation :



Copper sulphate is prepared on the large scale by the action of dilute sulphuric acid on copper in the presence of air :



or by the "weathering" of copper pyrites, which may first be roasted :



Commercial cupric sulphate usually contains ferrous sulphate, with one hydrated form of which $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ it is isomorphous and forms mixed crystals. If the solution contains a considerable amount of copper, the crystals consist of $(\text{Cu}, \text{Fe})\text{SO}_4 \cdot 5\text{H}_2\text{O}$; if the iron predominates they have the composition $(\text{Fe}, \text{Cu})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Similar results are obtained with zinc sulphate. The iron may be separated by boiling the copper sulphate solution with a little nitric acid, which oxidises ferrous to ferric sulphate, this remaining in the mother liquor on crystallisation.

The solubilities of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in g. $\text{CuSO}_4/100$ g. H_2O are :

0°	15°	25°	30°	50°	60°	80°	100°	104°
14.9	19.3	22.3	25.5	33.6	39.0	53.5	73.5	78.0

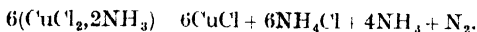
The salt $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is insoluble in alcohol and is precipitated in small crystals when alcohol is added to the solution. Several crystalline hydrates are known. On exposure to air the blue pentahydrate crystals effloresce to a pale blue powder of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, which is best made by exposing the pentahydrate over P_2O_5 in a desiccator at 25°–30° for about eleven days till the weight corresponds with trihydrate. The pentahydrate crystals at 100° crumble to a bluish-white powder of monohydrate $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. At 220°–260° this loses most of the combined water, but 0.04 per cent is retained even at 360°, and the salt begins to lose sulphur trioxide at higher temperatures before all the water is expelled. Anhydrous CuSO_4 is a white powder best prepared by heating powdered pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (made from electrolytic copper) in a U-tube at 240° in a current of dry air until the weight corresponds with CuSO_4 . If the material contains a trace of iron the product is discoloured.

Copper sulphate is stable to 653° but decomposes completely at 736° : $\text{CuSO}_4 = \text{CuO} + \text{SO}_3$. The white powder obtained by dehydration at 260° is used to detect water in alcohol, ether, etc., when it becomes blue. Anhydrous or hydrated copper sulphate absorbs hydrogen chloride gas and is decomposed by it at 400° or by the aqueous acid : $\text{CuSO}_4 + 2\text{HCl} = \text{CuCl}_2 + \text{H}_2\text{SO}_4$. This reaction may be applied in separating hydrochloric acid from other gases, such as sulphur dioxide.

Copper sulphate is used in making green pigments, as a mordant in dyeing, and in making *Bordeaux mixture* (a mixture of the solution and

milk of lime) as a wash to kill moulds and fungi on vines. The sulphate solution is also used in steeping wheat to prevent the growth of fungus.

If a solution of cupric sulphate is precipitated with ammonia and the precipitate dissolved in excess of ammonia, a deep-blue solution is formed. If a layer of alcohol is poured carefully over this solution in a cylinder, the latter corked to prevent evaporation, and the whole allowed to stand, long transparent deep-blue rhombic prisms of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ are deposited. Cupric chloride forms $\text{Cu}(\text{NH}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, which crystallises on cooling a hot solution of cupric chloride saturated with ammonia gas. Anhydrous cupric sulphate absorbs ammonia gas, forming a blue powder of $\text{CuSO}_4 \cdot 5\text{NH}_3$, which dissociates to form $\text{CuSO}_4 \cdot 4\text{NH}_3$ and $\text{CuSO}_4 \cdot 2\text{NH}_3$. Anhydrous cupric chloride absorbs ammonia gas forming $\text{CuCl}_2 \cdot 6\text{NH}_3$, which readily dissociates on heating, forming $\text{CuCl}_2 \cdot 4\text{NH}_3$, $3\text{CuCl}_2 \cdot 10\text{NH}_3$, and $\text{CuCl}_2 \cdot 2\text{NH}_3$. The latter on heating decomposes as follows :



The atomic weight of copper proved difficult to find exactly. Richards determined the ratios $\text{CuBr}_2 : 2\text{AgBr}$, and $\text{Cu} : \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (which gave a poor result), etc., and also compared the weights of copper and silver deposited by electrolysis. The valency follows from the atomic heat.

SILVER

History.—Silver was known in Predynastic Egypt (c. 4000 B.C.) but was very rare. A fine Chaldean silver vase of 2850 B.C. is in the Louvre. The oldest silver probably came from North Syria and Asia Minor, which were centres of Hittite civilisation. Silver mines in Spain were worked at an early date.

Occurrence.—Silver occurs native, occasionally nearly pure but usually containing copper and gold. Important ores are the sulphide *argentite* (or *silver glance*) Ag_2S (the commonest ore), *chlorargyrite* (or *horn-silver*) AgCl , *pyrargyrite* (or *ruby-silver*) Ag_3SbS_3 , *stromeyerite* (or *silver-copper glance*) $(\text{Cu}, \text{Ag})_2\text{S}$, and *stephanite* Ag_5SbS_4 . Less important are *proustite* Ag_3AsS_3 , *bromargyrite* AgBr , and *iodargyrite* AgI . Traces of silver occur in sea water. Most copper and lead ores contain small amounts of silver, which is extracted in copper refining (p. 721) and from argentiferous lead; silver is extracted from the ores of the Ontario cobalt mines, and in North America, Mexico, Peru, Bolivia, Broken Hill (N.S. Wales), and Japan.

Metallurgy.—Silver is extracted from its ores by several processes.

I. **The cupellation process**, the oldest, is mentioned in the Bible and is described by Strabo and by Pliny as in use in Spain. Lead from galena is nearly always argentiferous and forms an important source of silver, and the process is also used with alloys formed by smelting lead and silver ores together. The argentiferous lead is first "desilvered" by the Pattinson or Parkes process (see below) and the lead-silver alloy

rich in silver is then melted on a flat dish or *cupel* formed of bone-ash. A blast of air is driven over the surface of the molten metal (Fig. 364) when the lead is oxidised to lead monoxide or litharge PbO , which fuses and is swept off by the air blast. The last portions of litharge are absorbed by the porous cupel and a bright mass of silver is left.

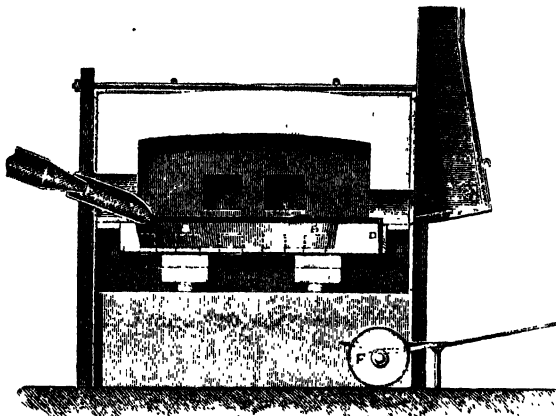


FIG. 364.—Cupellation furnace.

When the metal contains 60–70 per cent Ag the temperature is raised and a little sodium nitrate added to remove impurities. In the last stage of the process the litharge film becomes so thin that iridescent colours are seen; the bright silver surface then “flashes” out (an appearance sometimes called by the German name “blek”) and the metal contains 99.5 per cent of silver.

II. The Pattinson process (1833). On cooling fused argentiferous lead nearly pure lead separates. The crystals are removed by perforated iron ladles and the remaining liquid alloy becomes richer in silver. If the process were carried far enough, lead and silver would begin to separate out together at the eutectic point (2.5 per cent Ag). In practice seven-eighths of the lead are removed. The process is carried out in a row of ten iron pots, the lead separated being passed on from pot to pot to be remelted, and the liquid alloy passed in the other direction. The silver gradually accumulates in the alloy at one end of the series, and desilvered lead at the other. The rich alloy is then cupelled.

In the modification known as the Luce-Rozan process only two pots are used, a small upper melting pot and a large lower crystallising pot. The lead is deposited in the latter by blowing steam at 50 lb. pressure through the fused metal, whilst cold water is sprayed on the surface. When two-thirds of the lead have separated the liquid is strained off through a perforated plate. The separated lead is remelted and the process repeated until the proportion of silver mechanically retained in the lead crystals is sufficiently small. In this process any copper and antimony are removed from the lead.

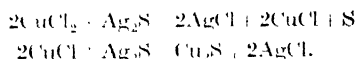
III. The Parkes process (1850). Molten lead dissolves only about 1 per cent of zinc and molten zinc only 1 per cent of lead. Silver, however, is soluble in zinc. One or two per cent of zinc is added to fused argentiferous lead at a temperature above the melting point of zinc, when the molten alloy of zinc and silver floats to the surface and solidifies on cooling. A second lot of zinc is then added. The crust is skimmed off with a perforated ladle and strongly heated with carbon in a fire-clay retort. Zinc distils leaving silver which is cupelled. A continuous process is also used. The Parkes is superseding the Pattinson process.

The zinc alloy may also be electrolysed (as anode) in zinc chloride solution; zinc is deposited on the cathode and silver is left. To remove traces of zinc dissolved in the lead, the latter is heated to redness and a blast of steam forced through it, when zinc oxide rises to the surface. Zinc is now often removed as chloride by treatment with chlorine.

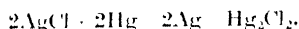
Any gold and copper present in the lead are also removed by the zinc. The desilvered lead contains only 0.0004 per cent of silver, whilst that obtained by the Pattinson process contains 0.001-0.002 per cent. If bismuth is present (which may be objectionable and is difficult to remove from the lead), it goes to the argentiferous part in the Pattinson process, but remains in the lead in the Parkes process.

IV. Amalgamation process. The amalgamation process has been used since 1557 in Mexico, where fuel is scarce, but is being replaced by the cyanide process (see below).

The ores containing metallic silver, silver chloride and sulphide and a large quantity of rock are finely crushed in stamping mills worked by mules, and the fine mud mixed with a little salt is then well trodden by mules on a paved floor or *patio*. Mercury is added together with a little roasted pyrites, containing cupric and ferric sulphates, and the treading is continued for fifteen to forty five days. Copper chlorides are probably first produced from the roasted pyrites and salt, and these decompose the silver sulphide with formation of silver chloride:



The silver chloride then dissolves in the salt brine and is reduced by the finely divided mercury:

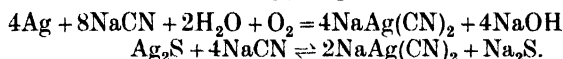


The silver amalgamates with the excess of mercury. About 1 per cent of sodium in the mercury prevents the formation of a fine powder, which would be lost in washing. The amalgam is separated by washing, the excess of mercury is pressed out in canvas bags, and the residue is distilled in iron retorts to recover the mercury.

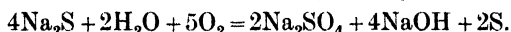
V. Wet processes (Percy and Patera, Augustin, Ziervogel, etc.). The ore is roasted either alone, when soluble silver sulphate is formed and can be lixiviated, and precipitated with copper, or with salt when silver chloride is produced which is extracted with hot common salt

solution or a solution of sodium thiosulphate, and the silver precipitated as silver sulphide by sodium sulphide.

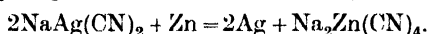
In the modern cyanide process the unroasted ore or concentrate, finely ground in ball mills, is leached with a dilute (0.4 per cent) solution of sodium cyanide, the slime being well agitated by a stream of air. Soluble sodium argentocyanide $\text{NaAg}(\text{CN})_2$ is formed :



The sodium sulphide is oxidised to sulphate by aeration :



The silver is precipitated from the solution by zinc :



Silver is now largely obtained from native silver in Mexico, the U.S.A. and Canada. Some comes from gold and copper refining, and from ores of other metals (copper, zinc, and lead).

Silver is refined by cupellation, or it if contains gold by the *Moebius process* by electrolysis in silver nitrate solution with about 1 per cent of free nitric acid ; the cathode is a plate of pure silver and the anode a block of the silver to be refined. Silver is deposited, copper dissolves, and the gold present in the anode deposits as a slime which is collected in a canvas bag.

Pure silver.—In order to obtain pure silver, the commercial alloy with copper is dissolved in dilute nitric acid, when copper and silver nitrates are formed. The solution is evaporated and diluted with water. Hydrochloric acid is added to precipitate silver chloride, which is filtered and washed with hot water till free from acid. Silver chloride is also formed by adding hydrochloric acid to laboratory "silver residues". Silver can be obtained from the chloride in several ways.

(a) The dry silver chloride is fused in a crucible with sodium carbonate, when a button of pure silver is formed :



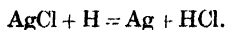
A crucible furnace should be used, as silver has rather a high melting point (960°).

(b) The moist silver chloride is boiled with sodium hydroxide solution and grape sugar, when the oxide first formed is converted into a grey powder of metallic silver, together with a dark-brown solution containing the oxidation products of the sugar :



The silver is well washed with boiling distilled water.

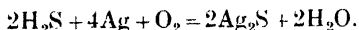
(c) Dilute sulphuric acid is poured over the moist silver chloride and a stick of pure zinc placed in the mixture. The chloride is reduced, forming a grey mass of silver powder (*molecular silver*), which is washed and dried



The silver from (b) or (c) may be fused in a crucible with sodium carbonate to form a button. (If silver is fused in a glazed porcelain crucible, the glaze becomes yellow, owing to the formation of silver silicate). Stas distilled the silver in a quicklime retort with the oxyhydrogen blowpipe. Richards showed that pure fused silver contains a little occluded oxygen, which may be removed by fusion on lime in an atmosphere of hydrogen, but the metal then contains a trace of calcium.

Properties of silver.—Silver is a pure-white metal, which conducts heat and electricity better than any other metal. The m. pt. is 960.5° in absence of air and 956° in air (when some oxide is formed). It boils at 1955° forming a pale-blue vapour, the density corresponding with the formula Ag. Silver is very malleable and ductile; it can be beaten into leaves 0.00025 mm. thick, which become somewhat transparent on heating. Very thin films deposited on glass transmit blue light.

Silver, like gold and platinum, is a "noble" metal, not oxidised in air at the ordinary temperature. On exposure to ordinary air it slowly tarnishes and becomes covered with an adherent film, which is yellow, blue and black with increasing thickness. This film is composed of silver sulphide Ag_2S , formed by the decomposition of hydrogen sulphide in the air in presence of oxygen:



The staining of silver spoons used with eggs is also due to the formation of silver sulphide from the combined sulphur in the albumin of the egg. The tarnish is readily removed by a dilute solution of potassium cyanide (*poisonous!*), followed by washing in plenty of water.

Fused silver dissolves up to 20 times its volume of oxygen, which is liberated as soon as the metal begins to solidify, when the metal "spits", part of the fused metal being forced out as globules or excrescences. This is a good test of the completion of cupellation. It is prevented by covering the metal with charcoal powder. Silver is attacked by chlorine, and more slowly by bromine, iodine and sulphur. It dissolves in hot concentrated hydriodic acid with evolution of hydrogen. It is not attacked by hydrochloric acid or dilute sulphuric acid, but is attacked by boiling concentrated sulphuric acid or cold dilute nitric acid. Silver resists the action of alkalis, even fused, hence silver crucibles are used for fusion with caustic alkalis, but may be replaced by those of pure nickel, although the latter is slightly attacked.

Silver deposited on glass by reduction is used in the manufacture of mirrors. This may be demonstrated as follows.

Clean a test-tube with boiling nitric acid, wash well with water, and prepare in it a dilute solution of silver nitrate. Add *dilute* ammonia drop by drop until the brown precipitate of silver oxide is *almost* redissolved. Then add potassium hydroxide solution and a solution of Rochelle salt

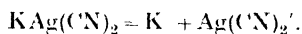
or grape sugar, which acts as the reducing agent. Place the tube in a beaker of hot water. A mirror of silver is deposited on the tube.

A *colloidal solution* of silver may be prepared by Bredig's method of striking an electric arc between silver wires under water. The metal is volatilised, and condensed in the water in the form of very small particles which remain in colloidal suspension. Colloidal silver is also formed by reduction with ferrous sulphate, etc., in presence of sodium citrate, when a red transparent solution is formed. Colloidal silver stabilised by alkaline albumin solution is called *protargol* and is a dark-brown liquid used as a disinfectant in ophthalmic cases.

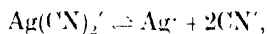
Commercial silver is alloyed with copper because the pure metal is too soft for coinage or jewellery work. The proportion of silver in 1000 parts of alloy is called the *fineness*. British silver has a fineness of 925, United States of 900. Cadmium alloyed with silver makes it easier to work.

Electroplating with silver.—The electrodeposition of silver is applied in the silver coulometer (p. 223).

Formerly, copper goods were plated by laying a strip of silver on a bar of clean copper, heating and rolling the bar to the required thickness. This is known as *Sheffield plate*, and the layer of silver is much thicker than with electroplated goods. Copper articles are electroplated with silver by making them the cathode in a solution of silver cyanide in excess of potassium cyanide, the anode being a plate of pure silver. The solution contains potassium argentocyanide :



The anion is very slightly dissociated :



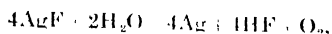
and the silver ions are deposited on the cathode as a coherent film of metal instead of the crystalline metal formed from silver nitrate solution. The cyanide ions discharged on the silver anode form silver cyanide, which dissolves in the solution. The net result is the transfer of silver from the anode to the cathode. Bright deposits are formed if carbon disulphide is added to the solution. A compound of silver nitrate and thiourea can be used instead of cyanide.

SILVER COMPOUNDS

Silver in its ordinary compounds is univalent, but a few compounds of bivalent silver are known. Unlike copper, it does not form basic salts. The silver salts are ionised in solution. The test for the silver ion is the formation of a white curdy precipitate of silver chloride AgCl , insoluble in dilute nitric acid but readily soluble in ammonia, potassium

cyanide or sodium thiosulphate. Complex compounds which give only a few silver ions are formed in these solutions.

Silver fluoride AgF is the only halogen compound of silver appreciably soluble in water. Hydrofluoric acid does not act on the metal, but dissolves the oxide. The fused salt, which contains metallic silver :

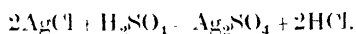


is an *elastic* black mass, easily cut with scissors. Acid fluorides AgHF_2 and AgH_3F_4 are described.

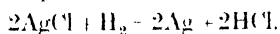
Silver subfluoride Ag_2F , which is bright yellow, crystalline and electrically conducting, is formed by heating a solution of AgF with silver powder, or by the electrolysis of AgF . It has a characteristic X-ray spectrum.

Silver chloride AgCl occurs native as *horn-silver* or *chlorargyrite*. It is prepared by adding hydrochloric acid or a chloride to a solution of silver nitrate : it readily fuses (m. pt. 455°) to a dark-yellow liquid which solidifies on cooling to a soft, colourless, tough mass, described as *argentum cornu* by Conrad Gesner (1565), by Matthesius (1585) as "glass-ore, transparent like horn in a lantern", and as *luna cornea* by Oswald Croll (1608), who says it was used by the alchemists in the fraudulent transmutation of lead into silver. Silver chloride boils at 1550°, the vapour density corresponding with AgCl . The fused chloride according to Stas is quite insoluble in cold water, but the curdy precipitate is slightly soluble. It dissolves slightly in dilute nitric acid on standing, dissolves in 200 parts of concentrated hydrochloric acid, is fairly easily soluble in sodium chloride solution, and dissolves readily in dilute ammonia, forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$, and in solutions of potassium cyanide and sodium thiosulphate. Solid silver chloride absorbs ammonia, forming $\text{AgCl} \cdot 3\text{NH}_3$, $2\text{AgCl} \cdot 3\text{NH}_3$, and other compounds. The thiosulphate solution contains a stable complex ion $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, and **sodium silver thiosulphate** $\text{Na}_4[\text{Ag}_2(\text{S}_2\text{O}_3)_3]$ or $\text{Na}_5[\text{Ag}_3(\text{S}_2\text{O}_3)_4]$ separates in crystals on adding alcohol or evaporation in a vacuum. It has a strong sweet taste (*poisonous!*).

Silver chloride is not decomposed by cold concentrated sulphuric acid, but the boiling acid dissolves it :



It is reduced on heating in hydrogen (silver iodide is only incompletely reduced even at high temperatures) :



Silver bromide AgBr forms a pale-yellow precipitate insoluble (like the chloride) in dilute nitric acid, and only sparingly soluble in *dilute* ammonia but readily in concentrated ammonia. It does not absorb ammonia gas, but liquid ammonia converts it into $\text{AgBr} \cdot 3\text{NH}_3$.

Silver iodide AgI is formed as a light-yellow precipitate, insoluble in dilute nitric acid and only sparingly soluble even in concentrated

ammonia (which changes its colour to white), but soluble in sodium thiosulphate solution, hydriodic acid, and saturated potassium iodide solution. Silver iodide exists in three different crystalline forms. From -10° to 72° it *contracts* on heating.

Compounds of silver and thallos halides (which do not form mixed crystals) known are 2AgCl , 3TlCl and 2AgBr , 3TlBr .

Silver chlorate AgClO_3 is soluble and is formed by dissolving silver oxide in chloric acid and crystallising, or by passing chlorine into a suspension of silver oxide in water, filtering and evaporating :



It decomposes on heating into chloride and oxygen, and a trace of chlorine. It is reduced by sulphurous acid : $\text{AgClO}_3 + 3\text{SO}_2 + 3\text{H}_2\text{O} = \text{AgCl} + 3\text{H}_2\text{SO}_4$. **Silver perchlorate** AgClO_4 is soluble in water and in benzene. **Silver bromate** and **iodate** are formed by precipitation since, unlike the chlorate, they are sparingly soluble.

Silver oxide Ag_2O is obtained by precipitating a solution of silver nitrate with sodium hydroxide solution, filtering, washing and drying the brown precipitate at 60° , when it is almost black :



The hydroxide AgOH is said to be precipitated from alcoholic silver nitrate solution by alcoholic potash at -30° , but it is very unstable, passing into the oxide. Silver oxide may also be obtained by boiling silver chloride with sodium hydroxide solution. Silver oxide is slightly soluble in water (0.03 gm. per litre), forming a solution alkaline to litmus, and the moist solid readily attracts carbon dioxide from the air.

Silver oxide cannot be completely freed from water. It is completely decomposed on heating at 300° into silver and oxygen. It is said to be formed by heating finely divided silver at 300° in oxygen under 15 atm. pressure. It is used as a base and as an oxidising agent in organic chemistry and for giving a yellow colour to glass, a yellow silicate Ag_2SiO_3 being formed. When the oxide is dissolved in ammonia and the solution exposed to the air, a black precipitate containing **silver nitride** Ag_3N is deposited, which is very explosive when dry, and is called *fulminating silver*.

Silver suboxide Ag_4O is formed by the action of steam at 180° on the subfluoride Ag_2F .

Silver carbonate Ag_2CO_3 is a light-yellow powder (white when pure) formed by precipitating silver nitrate solution with an alkali carbonate, or preferably a mixture of carbonate and bicarbonate ; it decomposes on heating into silver, oxygen and carbon dioxide. With excess of potassium carbonate, a white double carbonate KAgCO_3 crystallises on cooling a hot concentrated solution. Moist silver oxide absorbs carbon

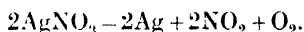
dioxide to form silver carbonate. Silver carbonate is sparingly soluble and is almost completely hydrolysed in solution.

Silver acetylide Ag_2C_2 is an explosive white solid precipitated by acetylene from ammoniacal silver nitrate solution.

Silver cyanide AgCN is formed as a white precipitate from a silver salt and cyanide solutions; it dissolves in excess of cyanide to form the complex ion $\text{Ag}(\text{CN})_2^-$, salts of which, $\text{KAg}(\text{CN})_2$, etc., and also the free acid $\text{HAg}(\text{CN})_2$, are known in the solid form. **Silver thiocyanate** AgCNS is formed as a very insoluble white cheese-like precipitate, insoluble in nitric acid but soluble in KCNS solution, forming the complex salts $\text{KAg}(\text{CNS})_2$, $\text{K}_2\text{Ag}(\text{CNS})_3$ and $\text{K}_3\text{Ag}(\text{CNS})_4$.

Silver nitrate AgNO_3 is the most important silver salt. It is made by dissolving silver in hot dilute nitric acid, evaporating and crystallising, when colourless transparent rhombic crystals are formed, which are very soluble in water. It is also soluble in alcohol, pyridine, etc. The salt readily fuses (m. pt. 209°) and when cast into sticks forms *lunar caustic*. Silver nitrate is readily decomposed by organic matter such as paper, cork or the skin, deep-black metallic silver being deposited, so that a solution of silver nitrate is used as an indelible ink for marking linen. The black stain can be removed by a dilute solution of potassium cyanide.

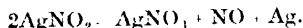
Silver nitrate decomposes at 450° , when oxygen and nitrogen dioxide are evolved and silver remains:



The decomposition point is much higher than that of copper nitrate, so that this may be separated from silver nitrate by heating, adding water, and filtering from the copper oxide.

Solid silver nitrate absorbs ammonia gas with evolution of heat and forms a compound $\text{AgNO}_3 \cdot 3\text{NH}_3$. If ammonia is added to a solution of silver nitrate until the silver oxide first precipitated is dissolved, and the liquid is evaporated out of contact with air, crystals of a compound $\text{AgNO}_3 \cdot 2\text{NH}_3$ separate. Double salts, e.g. $\text{AgNO}_3 \cdot \text{NH}_4\text{NO}_3$ and $\text{AgNO}_3 \cdot \text{KNO}_3$, are known.

Silver nitrite AgNO_2 is formed as a yellowish-white precipitate when solutions of silver nitrate and sodium nitrite are mixed. It may be crystallised from hot water. It decomposes on heating, evolving nitric oxide and leaving silver nitrate and silver:

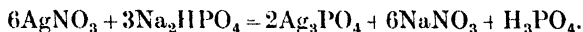


Silver phosphide Ag_3P_2 is formed from the elements on heating.

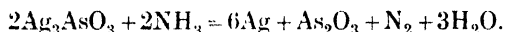
Silver orthophosphate Ag_3PO_4 is formed as a pale-yellow precipitate when a solution of sodium phosphate is added to one of silver nitrate. The reaction is usually represented by the equation:



but as the precipitate is readily soluble in nitric acid, only about two-thirds of this amount of silver is precipitated :

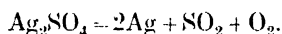


Silver hydrogen phosphate Ag_2HPO_4 is deposited in white crystals from a solution of the phosphate in phosphoric acid. **Silver metaphosphate** AgPO_3 and **pyrophosphate** $\text{Ag}_4\text{P}_2\text{O}_7$ are white precipitates formed by adding silver nitrate to solutions of the corresponding sodium salts. **Silver arsenite** Ag_3AsO_3 and **silver arsenate** Ag_3AsO_4 are canary-yellow and light chocolate-brown precipitates, respectively. The arsenite dissolves in ammonia, and if the solution is boiled silver is deposited :



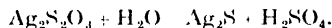
Silver sulphide Ag_2S is a black solid formed when silver is heated with sulphur or in hydrogen sulphide, or silver nitrate solution is precipitated with hydrogen sulphide. It is insoluble in ammonia and sodium thiosulphate solution, but dissolves in potassium cyanide solution and in hot dilute nitric acid.

Silver sulphate Ag_2SO_4 is formed by boiling silver with concentrated sulphuric acid, or by precipitating a solution of the nitrate with dilute sulphuric acid. It is sparingly soluble in water, but dissolves readily in dilute nitric acid or concentrated sulphuric acid. Silver sulphate decomposes at a red heat :



Silver hydrogen sulphate AgHSO_4 is formed in light-yellow crystals when the sulphate is dissolved in less than three parts of sulphuric acid.

Silver thiosulphate $\text{Ag}_2\text{S}_2\text{O}_3$ is formed as a precipitate on mixing equivalent amounts of silver nitrate and sodium thiosulphate in solution. It is difficult to obtain pure (when it is white), and decomposes when boiled with water :



Photography.—The blackening of silver chloride on exposure to light was observed by Boyle, who explained it as due to the action of air. Scheele (1777) showed that if the blackened substance is digested with ammonia, unchanged silver chloride is dissolved and a residue of silver remains. He also noticed that violet light acts most strongly on the chloride, whilst red and orange light have practically no action.

The first to turn the sensitive silver salts to account in making light pictures, or photographs, was Thomas Wedgwood (1802). In 1839 Daguerre allowed iodine vapour to act on a polished silver surface, which was exposed in the camera, and an invisible image was produced. The treated plate was exposed to mercury vapour, which condensed only on the portions which had been acted upon by light, leaving the unaltered iodide in the shadows. The iodide was removed by a solution of sodium

thiosulphate, as suggested by Herschel, and the picture thus fixed or rendered non-sensitive to light. Archer (1851) used a transparent film of collodion spread on glass, and impregnated with zinc or cadmium bromide or iodide. This was treated before use by immersion in a solution of silver nitrate, when the halide was deposited. The plate was exposed in the camera whilst still wet, and then developed (Talbot, 1839) by immersion in a solution of a reducing agent such as pyrogallic acid, which converted the *altered* halide into black metallic silver. The *unaltered* halide was then dissolved out by potassium cyanide or sodium thiosulphate, and a negative produced, in which the light and shade in the picture are reversed. Positives were obtained by laying the negative on a piece of paper coated with silver chloride, and then exposing for some minutes to sunlight or bright daylight, when the chloride was sufficiently changed in colour to give a positive "print." The print could be fixed in the same way as the plate, when a yellowish silver image was left. The colour was much improved by immersing the print, before it was fixed, in a solution of gold chloride (brown to purple tones), or potassium chloroplatinate (grey tone), some of the silver being dissolved and replaced by the nobler metal.

In the modern process the light-sensitive medium is usually a suspension or "emulsion" of silver halide in gelatin. The halide used depends on the particular type of photographic material. High-speed plates and films contain a mixture of bromide with a small proportion of iodide: process plates, fast lantern plates and bromide paper contain bromide: warm tone "chlorobromide" papers and lantern plates contain a mixture of chloride and bromide: gaslight papers and lantern plates contain chloride. Self-toning print-out papers usually have a collodion emulsion containing silver chloride, silver citrate, gold chloride and citric acid. The various types of gelatin emulsion are prepared by adding silver nitrate to a solution of gelatin in hot water containing alkali halides in the required proportions. The warm emulsion, after "ripening" for some time, when the silver halide grains increase in size, is allowed to cool and set. The jelly is cut up, washed with water to remove soluble salts, and is then remelted and coated as a thin film on glass (for "plates"), celluloid (for "films"), or on paper having a specially prepared surface. All operations are carried out in the dark, or in light of a colour to which the photographic material is not sensitive. By adding certain dyes ("sensitizers") to the photographic emulsion, it is possible to make it sensitive to rays which do not affect ordinary photographic materials: thus erythrosine makes the emulsion sensitive to yellow and green in addition to the blue and violet rays ("orthochromatic"), some cyanine derivatives confer sensitivity to the whole visible spectrum ("panchromatic") and other cyanine derivatives make the emulsion sensitive to the near infra-red region, rays which are capable of penetrating fog and haze well enough to render long-distance photography possible.

After exposure in the camera, which may be only a small fraction of a second, the film or plate does not change in appearance, but in reality a change has occurred in the places on which light has fallen. It is *developed* by immersing in a solution of a reducing agent such as pyro-

gallol, hydroquinone, or metol, in the presence of alkali and sodium sulphite. The exposed silver halide is then reduced to black metallic silver: $C_6H_4(OH)_2 + 2AgBr = C_6H_4O_2 + 2Ag + 2HBr$.

To prevent over-vigorous development, when some of the unexposed halide is reduced and leads to "fogging" of the plate, potassium bromide is added to the developer. It retards development by lowering the solubility of the silver bromide or chloride. Desensitizers are dyes (usually of the safranin class) which when dissolved in the developer solution enable development to be carried out in fairly bright artificial light instead of the very dim red or green light usually employed. After washing, the film or plate is fixed in a solution of sodium thiosulphate. Positive prints are usually made on bromide or gaslight papers, which are exposed, developed, and fixed in the same way as plates.

Sheppard (1925) found that the very high speed of photographic emulsions is due to the presence of traces (1 part in 100,000 to 1 part in 300,000) of organic sulphur compounds present in the gelatin. The exact mechanism of the photochemical changes is still obscure. According to one theory, a subhalide, e.g. Ag_2Br , is formed by the transfer of bromine to the sensitizer. Later work points, however, to a purely physical explanation (Joly, 1905). Halides of silver on exposure to light emit electrons, and the photosensitiveness is in the ratio of the order of the photo-electric effect: $AgBr > AgCl > AgI$. Cathode rays (free electrons) and X-rays (which produce free electrons from matter) also produce photographic effects. Sheppard and Trivelli (1926-1928) consider that minute nuclei of silver and silver sulphide ("sensitivity specks") which are present in silver halide crystals, play an important part, electrolytic action being set up on exposure to light which enlarges the nuclei so that they may become centres of development. Toy and Harrison (1928) found that the electrical conductivity of silver halides increases on exposure to light, and suggest that on exposure the halogen ions lose their extra electron, which is thus free to convert a silver ion to a silver atom. The quantum efficiency of the process (p. 216) is 1 (Eggert and Noddack, 1923): the primary process is confined to the halide ion: $Hal^- = Hal + e^-$, followed by the secondary reaction $Ag^+ + e^- = Ag$. According to Hamburger (1933) as few as three silver atoms, arranged as in the silver crystal lattice, are able to act as a centre from which development may proceed. It seems to be well established that photosensitivity depends to some extent on the nature of the adsorbed gelatin-silver or dye-silver complex on the surface of the halide crystals. Scheele's original experiments, however, prove conclusively that chemical reactions occur when the light is prolonged, and loss of chlorine with the formation of silver (not subhalide) has been established by experiments with the microbalance (Hartung, 1922-25). Up to 95 per cent may be decomposed. Rehalogenation restores the original weight and colour.

Bivalent silver.—Apart from the oxide Ag_2O and difluoride Ag_2F_2 , no simple compounds of bivalent silver are known, but some dark-coloured coordination compounds of salts of bivalent silver have been prepared. Since the ion has the same outer electronic structure as the cupric ion they are paramagnetic. Some compounds are isomorphous with compounds of bivalent copper and cadmium.

Argentio fluoride AgF_2 is formed by the action of fluorine on silver powder (Ruff, 1934). **Argentio oxide** Ag_2O is formed (i) by the action of boiling water on the compound $\text{Ag}_7\text{NO}_{11}$ (which may contain argentic nitrate) formed in black crystals on the anode in the electrolysis of silver nitrate solution; (ii) by precipitating silver nitrate solution with potassium or sodium persulphate (ammonium persulphate reacts differently); (iii) by oxidising Ag_2O with hot alkaline permanganate solution. It was thought to be silver peroxide Ag_2O_2 , but Barbieri showed that its solution in concentrated nitric acid does not reduce MnO_2 , PbO_2 or KMnO_4 , and oxidises iodine to periodic acid.

Anodic oxidation of silver nitrate in presence of pyridine gives the orange-red compound of **argentio nitrate** $[\text{Ag py}_4](\text{NO}_3)_2$, and a series of compounds containing dipyridyl $[\text{Ag dipy}_2]\text{X}_2$, where $\text{X} = \text{NO}_3$, HSO_4 , $\frac{1}{2}\text{S}_2\text{O}_8$, ClO_3 and ClO_4 , and other coordination compounds, are known.

By anodic oxidation of a solution of Ag_2O in nitric acid the oxide Ag_2O_3 of *trivalent silver* is formed (Barbieri, 1931), and this seems to be contained in the black oxide precipitated with persulphate (Yost, 1926).

GOLD

History.—Gold occurs in the free state and with its marked colour and brilliance was probably one of the first metals known to man. Gold ornaments are found in neolithic remains.

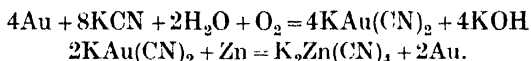
Occurrence. Gold usually occurs native, alloyed with a certain amount of silver and sometimes copper and traces of platinum. Some tellurium compounds of gold occur in small amounts, and traces of gold are found in all igneous rocks, in pyrites and other ores, and in sea water (less than $\frac{1}{30}$ th grain per ton). Gold is recovered from burnt pyrites.

Electrum is a native alloy of gold and silver, containing 15 to 45 per cent of silver; *green gold* contains 10 per cent of silver. These alloys were used in ancient Egypt and called *asem*. Australian gold sometimes contains an appreciable amount of silver and is pale in colour.

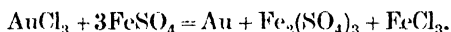
Metallurgy.—The gold sometimes occurs in isolated "nuggets" or grains in sands or alluvial gravels, or else in hard quartz "reefs". The gravels are broken up by powerful jets of water, and the rock is crushed in stamping mills or usually in ball-mills. By modern processes, quartz containing only 0.001 per cent, and gravels containing only 0.00003 per cent, of gold can be profitably worked. From the gravel washing, grains of gold are separated by passing the mud through long wooden troughs with battens across the bottom, or over blankets, which catch the heavier gold particles, the particles of rock being washed away. The slime from mills is sometimes passed over amalgamated copper plates, when the gold adheres to the mercury, but the *cyanide process* (MacArthur and Forrest, 1887) is now generally used and can be applied to finely stamped ore or "tailings" from other processes.

The material is percolated in large vats with false bottoms with a weak solution of potassium or sodium cyanide in which, when exposed

to air, the gold dissolves. The solution containing the complex aurocyanide $\text{KAu}(\text{CN})_2$ is reduced by adding charcoal or passing through boxes containing thin zinc shavings (the packages in which the cyanide is exported supply the zinc), when gold is precipitated as a black mud. The powder is fused in graphite crucibles and sent for refining :



Auriferous pyrites or "concentrates" are treated by Plattner's *chlorine process*; they are roasted, moistened with water and exposed to chlorine gas in tubs with false bottoms, when gold dissolves as trichloride AuCl_3 . This is washed out with water and the solution reduced with charcoal or ferrous sulphate :



Bromine water is now often used instead of chlorine.

The gold bullion is *refined* in various ways. If it contains silver it may be boiled with nitric or concentrated sulphuric acid, which dissolves the silver, provided the alloy does not contain more than one-third its weight of gold; if it contains more gold it is melted with silver to form an alloy which contains one-quarter its weight of gold, hence the process is called "quartation".

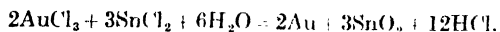
In the Miller process, used at the Ottawa Mint, chlorine gas is passed through the melted metal covered with borax, when silver chloride is formed and floats to the top. In an electrolytic process, the gold bullion is made the anode in gold chloride solution containing hydrochloric acid, pure gold being deposited on the cathode.

Properties.—Gold is a bright-yellow metal of high density and is a good conductor of heat and electricity. Its melting point (1063°) lies between those of silver (961°) and copper (1083°). Gold is the most ductile and malleable of all metals; it can be beaten into leaves less than 0.0001 mm. thick by first beating between sheets of vellum and finally between sheets of gold-beater's skin. Gold leaf transmits green light, which is seen by holding burning magnesium behind gold leaf between two sheets of glass. Deposits on gold lace are only 0.000002 mm. thick but still show the metallic lustre.

Gold is not attacked by oxygen at any temperature nor by single acids except selenic and iodic. It dissolves in chlorine water or in *aqua regia* (a mixture of concentrated nitric and hydrochloric acid which liberates chlorine). It is attacked by fused alkalis (unlike silver) and by fused nitre. Gold compounds are very easily reduced to the metal.

Colloidal gold is formed by Bredig's process (p. 738) or by reducing a solution of gold chloride with phosphorus, ferrous sulphate, formaldehyde, etc. The solutions are ruby-red when the gold particles are very fine, and blue with coarser particles; the red solutions are more stable in presence of a little gelatin. By precipitating gold chloride solution with stannous chloride, a purple powder called *purple of Cassius* (discovered by Andre-

Cassius and described in 1684) is thrown down ; according to Moissan this is a colloidal form of stannic oxide with adsorbed colloidal gold :



It is used in making gold ruby glass ; the glass when fused with the powder is at first colourless, but the red colour develops on annealing.

Gold is too soft for use in the pure state, so that it is alloyed with copper or silver, or both. Copper makes the metal redder, silver makes it pale. These alloys are malleable. Traces of lead and bismuth make gold brittle ; a purple alloy containing AuAl_2 is formed with aluminium.

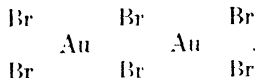
The " fineness " of a gold alloy is often expressed in " carats ", pure gold being 24 carat fine and standard alloys are 22, 18, 15, 12 and 9 carat, containing these proportions of gold in 24 parts. The alloy is " assayed " by cupellation with lead, the button containing gold and silver being then " parted " by flattening, heating with nitric acid to dissolve the silver, heating to redness and weighing on an assay balance.

Gold plating is carried out in the same way as silver plating by deposition from a bath containing gold cyanide dissolved in potassium cyanide, the requisite amounts of copper and silver being added, when these metals are deposited with the gold.

Gold coinage has almost entirely gone out of use, the metal being stored in ingots in vaults as a standard of value. The great rise in price of gold has made it profitable to work deeper and poorer lodes than was formerly thought possible.

GOLD COMPOUNDS

Gold forms aurous compounds AuX , all sparingly soluble, in which it is univalent, and the more important auric compounds AuX_3 in which it is trivalent. Compounds (AuCl_2 , AuBr_2 , AuO , AuS , AuSO_4) apparently containing bivalent gold may contain uni- and trivalent gold, $\text{Au}[\text{AuCl}_4]$, etc. Gold shows a marked tendency to covalency with a coordination number of 4 in auric compounds, *e.g.* gold tribromide is probably :



Gold dissolves in aqua regia to a bright yellow solution which on evaporation deposits deliquescent yellow crystals of chloroauric acid $\text{HAuCl}_4 \cdot 3$ or $4\text{H}_2\text{O}$ (commonly called " gold chloride "), soluble in water, alcohol and ether. This loses hydrogen chloride at 120° to form deep-red crystalline auric chloride AuCl_3 , which is also formed on evaporating a solution of gold in chlorine water and heating at 150° .

Chloroauric acid is easily reduced in solution to metallic gold by hydrogen gas or exposure to light. It forms salts, *e.g.* light-yellow crystals of $\text{KAuCl}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ on mixing with concentrated hydrochloric acid and potassium chloride.

At 175° AuCl_3 decomposes to a light-yellow powder of **aurous chloride** AuCl , which at higher temperatures is reduced to gold. Aurous chloride is insoluble but is decomposed by cold water: $3\text{AuCl} = \text{AuCl}_3 + 2\text{Au}$. On heating, KAuCl_4 forms the aurous compound KAuCl_2 .

Auric bromide AuBr_3 is formed in black crystals by dissolving gold in bromine. With potassium bromide it forms purple-red $\text{KAuBr}_4 \cdot 2\text{H}_2\text{O}$. At 115° AuBr_3 forms yellowish-grey or green **aurous bromide** AuBr , decomposed at a somewhat higher temperature into gold.

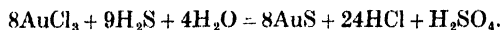
A green precipitate of **auric iodide** AuI_3 is formed on adding gold chloride solution to potassium iodide solution, but it soon decomposes into aurous iodide and iodine (*cf.* CuI_2). It dissolves in potassium iodide solution to form KAuI_4 , black crystals decomposed by heat with separation of gold. **Aurous iodide** AuI is formed as a yellow or greenish-yellow crystalline powder by the action of iodine on gold at 50°–114°, or the action of iodine in ether solution on gold. It is decomposed by heat and by water only on warming.

By the action of cold dilute alkali on aurous chloride a violet powder said to be **aurous hydroxide** AuOH is formed, which at 200° is said to form violet-grey **aurous oxide** Au_2O ; according to Pollard (1926) it is a mixture of gold and auric oxide Au_2O_3 . Aurous oxide or hydroxide is a very weak base.

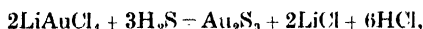
Auric hydroxide is formed as a reddish-brown powder by decomposing gold chloride (HAuCl_4) solution with alkali, or better with magnesium oxide or basic carbonate, and washing with dilute nitric acid (in which most of it dissolves). It is a very weak base, and also dissolves in hot potassium hydroxide solution, and on evaporation in vacuum pale-yellow needles of **potassium aurate** $\text{KAuO}_2 \cdot 3\text{H}_2\text{O}$ separate. Sodium aurate $\text{NaAuO}_2 \cdot \text{H}_2\text{O}$ is formed by fusing gold powder with sodium peroxide, dissolving and crystallising.

At 140°–150° auric hydroxide slowly forms **auric oxide** Au_2O_3 , and at higher temperatures metallic gold. (AuO is said to be formed at 155°–165°.)

Three gold sulphides are described. **Aurous sulphide** Au_2S is formed as a greyish-black precipitate on saturating a solution of potassium aurocyanide with hydrogen sulphide and adding hydrochloric acid to the clear solution. It dissolves in sodium polysulphide solution forming sodium sulphaurate NaAuS_2 (a compound of 3-valent gold). AuS , perhaps $\text{Au}^{\text{I}}[\text{Au}^{\text{III}}\text{S}_2]$, is precipitated by hydrogen sulphide from neutral gold chloride solution:



Auric sulphide Au_2S_3 is an amorphous black powder formed by the action of hydrogen sulphide at -10° on lithium chloraurate, $\text{LiAuCl}_4 \cdot 2\text{H}_2\text{O}$:



extracting the LiCl by alcohol, and drying at 70°. It is decomposed by water.

Gold when fused with sodium sulphide and sulphur forms a mass soluble in water and the solution on evaporation in vacuum deposits colourless crystals of **sodium sulphaurate** $\text{NaAuS}_2 \cdot 4\text{H}_2\text{O}$ (derived from Au_2S_3). Stahl (1715) fancifully suggested that Moses used this method to dissolve the Golden Calf!

The complex **sodium thiosulphaurite** $\text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2] \cdot \frac{1}{2}\text{H}_2\text{O}$ formed by the reaction: $\text{AuCl}_3 + 4\text{Na}_2\text{S}_2\text{O}_3 - \text{Na}_3[\text{Au}(\text{S}_2\text{O}_3)_2] + \text{Na}_2\text{S}_4\text{O}_6 + 3\text{NaCl}$, crystallises in colourless needles and is used in medicine as *sauochrysin* (Greek *chrysos*, gold). It is not reduced by ferrous sulphate, oxalic acid or stannous chloride.

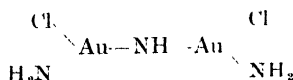
Potassium aurocyanide $\text{KAu}(\text{CN})_2$ is an important compound, formed when gold dissolves in potassium cyanide solution in presence of oxygen and on dissolving fulminating gold (see below) in boiling potassium cyanide solution, separating on cooling in colourless crystals. On evaporating a solution in hydrochloric acid and washing the residue, yellow **aurous cyanide** $\text{Au}(\text{CN})$ remains. Colourless crystals of **potassium auricyanide** $\text{KAu}^{\text{III}}(\text{CN})_4 \cdot \frac{3}{2}\text{H}_2\text{O}$ deposit on cooling a hot concentrated solution of auric chloride and potassium cyanide: it is not reduced by ferrous sulphate.

The ion $\text{Au}^{\text{III}}(\text{CN})_4^-$ containing tervalent gold is (like AuCl_4^- and AuBr_4^-) planar, but the isomeric ion $\text{Au}^{\text{I}}(\text{CN})_4^{3-}$ of univalent gold is (like $\text{Cu}(\text{CN})_4^{3-}$ and $\text{Zn}(\text{CN})_4^{2-}$) tetrahedral.

Oxysalts of gold are very uncommon. Besides the sulphates AuSO_4 and $\text{Au}_2(\text{SO}_4)_3$ (probably $(\text{AuO})\text{HSO}_4$) there is an **acid nitrate** $\text{H}[\text{Au}(\text{NO}_3)_4] \cdot 3\text{H}_2\text{O}$ (which forms crystalline salts), basic nitrates, and a fairly stable yellow crystalline **selenate** $\text{Au}_2(\text{SeO}_4)_3$ separating from a solution of gold in hot selenic acid.

The supposed compounds of *bivalent gold* are now usually regarded as complex compounds containing univalent gold in the cation and tervalent gold in the anion, e.g. AuCl_2 is $\text{Au}^{\text{I}}[\text{Au}^{\text{III}}\text{Cl}_4]^-$, etc.

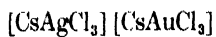
Fulminating gold is an olive-green powder of rather variable composition formed by digesting auric oxide or hydroxide with ammonia. When dry it detonates violently when heated or struck, forming gold, nitrogen, ammonia and steam. Raschig (1886) formulated fulminating gold as $\text{HN}=\text{Au} \cdot \text{NH}_2 \cdot \frac{3}{2}\text{H}_2\text{O}$. It is also precipitated by ammonia from gold chloride solution and then contains some chlorine. According to Weitz (1915) this fulminating gold is



with chlorine partly replaced by OH. Its explosibility is increased on washing with ammonia, when perhaps $[\text{Au}(\text{NH}_3)_2(\text{OH})_2]\text{OH}$ is formed. By the action of ammonia on aurous oxide **sesquiauramine** NAu_3NH_3 is formed, which on boiling with water forms **aurous nitride** Au_3N .

A delicate test for gold is to pour the boiling solution into a little concentrated stannous chloride solution, when the precipitated stannous hydroxide has a purplish colour if traces of gold are present.

A sparingly soluble caesium silver gold chloride, $\text{Cs}_2\text{AgAuCl}_6$ or



is used in the microchemical detection of caesium.

CHAPTER XXXVIII

THE ALKALINE-EARTH METALS

THE elements of Group II in the Periodic Table are all metals. They are divided into two sub-groups, the odd series and the even series, and usually as follows :

- (a) Even series : beryllium, mag- (b) Odd series : zinc, cadmium and
nesium, calcium, strontium, mercury,
barium and radium.

In most ways beryllium and magnesium resemble more closely the metals of the (b) series and will be described with them. Radium has been described in Chapter XXIII.

All these metals are bivalent. The so-called cadmous salts (Cd_2O , CdCl) are mixtures of bivalent cadmium compounds and finely divided metal. The mercurous salts such as calomel, in which the metal seems to be univalent, HgCl , have the doubled formulae Hg_2X_2 , in which the group $-\text{Hg}-\text{Hg}-$, made up of two bivalent mercury atoms, is also bivalent. All the metals form stable basic oxides MO and (except mercury) hydroxides $\text{M}(\text{OH})_2$. There is a regular increase in the solubility of these hydroxides in series (a) with increase in atomic weight, those of series (b) are practically insoluble in water.

The older chemists gave the name *earth* to all non-metallic substances insoluble in water and unchanged by fire. Lime and magnesia were found to have an alkaline reaction and were called *alkaline earths*, the name being afterwards applied to baryta and strontia. The alkaline earth metals were isolated by Davy in 1808 by the electrolysis of solutions of the chlorides with a mercury cathode, and distilling the amalgams so formed. Lavoisier had suggested that, like other "bases", the earths were oxides of metals. The metals were obtained in a coherent form by Bunsen and Matthiessen in 1855-6 by electrolyzing the fused chlorides with a carbon anode and a thin iron wire cathode.

The metals of the alkaline earths are all silver-white, oxidise in the air and decompose water, though less vigorously than the alkali metals. Calcium, strontium and barium form hydrides MH_2 , and true peroxides MO_2 in which the metal is bivalent (p. 197). The alkaline-earth metals, and also magnesium combine directly with nitrogen, forming nitrides M_3N_2 . Their compounds give distinctive colours when moistened with hydrochloric acid and heated on platinum wire in the Bunsen flame :

calcium, orange-red; strontium, crimson; barium, apple-green; radium, carmine-red.

The physical properties of elements of the even series (except radium) are :

	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electron configuration	2.2	2.8.2	2.8.8.2	2.8.18.8.2	2.8.18.18.8.2
Density	1.84	1.74	1.55	2.54	3.78
Atomic volume	4.90	13.97	25.9	34.5	36.7
Melting point	1280°	651°	851°	800°	710°
Boiling point	1500°	1100°	1439°	1366°	1537°

CALCIUM

History.—The history of the chemistry of limestone and quicklime has been dealt with in Chapter V.

Metallic calcium.—Metallic calcium was discovered by Davy in 1808. It is prepared on a technical scale by the electrolysis of fused calcium chloride.

The cathode is an iron or a water-cooled graphite rod which touches the surface of the fused chloride (Fig. 365). The cathode is slowly screwed up as the calcium accumulates and the metal is drawn out into the form of an irregular rod, protected from oxidation by a layer of chloride. A mixture of 100 parts of calcium chloride and 16.5 parts of fluorspar, which melts at a lower temperature (660°) than pure calcium chloride (782°) has been used as an electrolyte.

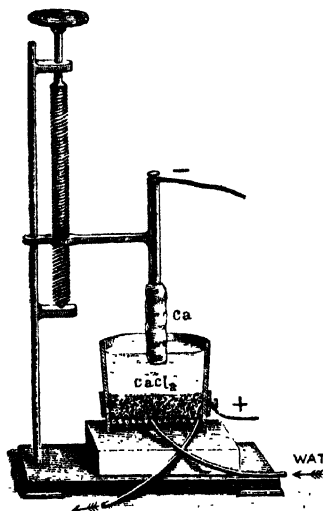
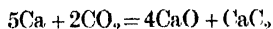


Fig. 365.—Calcium by electrolysis.

fluorides on heating, but not the iodides. When rapidly heated in carbon dioxide it forms calcium oxide and carbide :

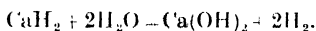


Calcium oxidises slowly in moist air and decomposes cold water slowly, evolving hydrogen, and calcium turnings are used to free absolute alcohol from the last trace of water.

Metallic calcium is used in hardening lead, debismuthising lead (Betterton process), deoxidising copper, iron, and steel, desulphurising petroleum, and reducing oxides of beryllium, thorium, chromium, and uranium. An alloy with aluminium has been used.

CALCIUM COMPOUNDS

Calcium hydride CaH_2 is a white solid formed with incandescence on heating calcium in hydrogen: it is stable in air but is violently decomposed by cold water, with evolution of hydrogen:



Calcium fluoride CaF_2 , which occurs native as *fluorspar*, is nearly insoluble in water (0.015 gm./lit. at 18°) but the precipitated fluoride is more soluble in ammonia, ammonium salts and acids. When heated on charcoal before the blowpipe it evolves hydrofluoric acid and leaves calcium oxide.

A red calcium subfluoride Ca_2F_2 is formed by heating calcium fluoride with calcium above 1400°.

By dissolving limestone or marble in hydrochloric acid a solution of calcium chloride CaCl_2 is formed. This usually contains ferric chloride as impurity, and is yellow. A little chlorine water is added to oxidise any ferrous iron, then the solution is filtered and milk of lime added until the liquid is slightly alkaline. On boiling, ferric hydroxide is precipitated; the filtered liquid is neutralised with pure hydrochloric acid and evaporated to a syrup, when colourless very deliquescent crystals of the hexahydrate $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ separate on cooling. These dissolve in water with considerable lowering of temperature and the eutectic point is -55° . On heating the crystals at 200° water is evolved and a white porous deliquescent dihydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ remains, which is used for preparing solutions for refrigerators. If heated more strongly a porous mass of the anhydrous salt is formed, which is used in drying gases, etc. This fuses at 773° and forms a hard crystalline deliquescent mass on cooling. The product contains a little free lime unless fused in hydrogen chloride gas. Commercial calcium chloride is made from the residues of the ammonia-soda process (p. 692). The dihydrate and the anhydrous salt evolve heat when dissolved in water. Calcium chloride dissolves readily in alcohol. Anhydrous calcium chloride absorbs ammonia gas forming the compound $\text{CaCl}_2 \cdot 8\text{NH}_3$, which dissociates on heating, first forming $\text{CaCl}_2 \cdot 4\text{NH}_3$.

If a solution of 120 parts of CaCl_2 in 100 parts of water is cooled to 38° - 18° , a tetrahydrate, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, separates, which exists in two forms, α and β . At 45.3° , the stable α form gives $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; at 177.5° , $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ separates from the solution; at 260° , anhydrous CaCl_2 (Roozeboom, 1889).

A basic chloride $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is formed in needles by boiling calcium hydroxide with calcium chloride solution.

Homburg (1693) observed that freshly-fused calcium chloride is phosphorescent; Baldwin (1674) had noticed the same property with calcium nitrate. Perfectly pure salts are not phosphorescent; the property is due to the presence of traces of heavy metals, such as bismuth.

Calcium bromide CaBr_2 (m. pt. 730°) and calcium iodide, CaI_2 (m. pt. 740°) are similar to the chloride. The bromide forms $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$ and the iodide hydrates with 6 and $8\text{H}_2\text{O}$. Red calcium subchloride Ca_2Cl_3 and calcium subiodide Ca_2I_3 are formed by heating the chloride and iodide with calcium and rapid cooling. CaI_1 is said to be formed by heating CaI_2 and iodine at 70° – 80° , and in solution.

Calcium oxide CaO is usually made by decomposing calcium carbonate by heating to redness. It begins to decompose at 550° , evolving carbon dioxide and leaving calcium oxide or *quicklime*. In a closed vessel the decomposition stops at a certain pressure of the carbon dioxide, known as the dissociation pressure, which has a definite value at each temperature, and the system is then in equilibrium: $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$.

$t^\circ \text{C.}$	-	500	600	700	800	898	900	950
P_{CO_2} , mm. Hg.	-	0.11	2.35	25.3	168	760	773	1490

If the carbon dioxide is swept away by a current of air, dissociation goes on till the reaction is practically complete. Decomposition occurs still more easily in a current of steam. Lime-burning is carried out in a limekiln (Fig. 366) in which lumps of limestone are heated by flames and hot gas from burning coal in the base of the kiln.

Pure calcium oxide is prepared by heating Iceland spar (pure native calcium carbonate) with the blowpipe in a platinum crucible, with free access of air, until a little of the white opaque residue after cooling and addition of water no longer effervesces with acid. It is a white amorphous mass, density 3.3, which melts at about 2570° and can be boiled in the electric furnace, the vapour condensing in cubic crystals. Lime resists the temperature of the oxy-hydrogen blowpipe without more than sintering, and is used in making furnaces for fusing platinum. These consist of two blocks of lime, hollowed out, in the lower one of which the metal is placed, whilst the blowpipe is introduced through a hole in the upper block.

Calcium hydroxide (*slaked lime*) is made by the action of water on quicklime (p. 77): $\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 15.54 \text{ k. cal.}$ (Gunpowder may be kindled by the heat evolved in the reaction.) The lime combines with the water, and forms a fine, dry, white powder of calcium hydroxide. The hydroxide dissolves sparingly, producing *lime-water* (1.29 gm. of CaO per litre at 15° ; 0.67 at 80°). The solubility (as Dalton found) decreases with rise of temperature.

Calcium hydroxide is formed as a white precipitate by adding sodium hydroxide solution to a concentrated solution of calcium chloride: CaCl_2 :

$2\text{NaOH} \cdot \text{Ca}(\text{OH})_2 + 2\text{NaCl}$. With saturated solutions the mixture becomes solid ("the chemical miracle" of Francesco Lana, 1686). Six-sided crystals of calcium hydroxide are deposited by evaporating lime-water in a vacuum over sulphuric acid. Slaked lime, when heated to dull redness, loses water and is converted into quicklime: $\text{Ca}(\text{OH})_2 \cdot \text{CaO} + \text{H}_2\text{O}$. The dissociation pressures are 100 mm. at 350° and 760 mm. at 450° . A hydrate $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ is described.

Quicklime exposed to the air slowly absorbs moisture and carbon dioxide, crumbling to a powder of calcium hydroxide and carbonate, but it does not absorb dry carbon dioxide, nor does it react in the cold with chlorine, hydrogen sulphide, sulphur dioxide or nitrogen dioxide: hydrogen chloride reacts only slowly. Lime-water on exposure to air becomes covered with a crust of calcium carbonate. If this is broken it falls to the bottom, and another appears. In this way the whole of the lime is precipitated.

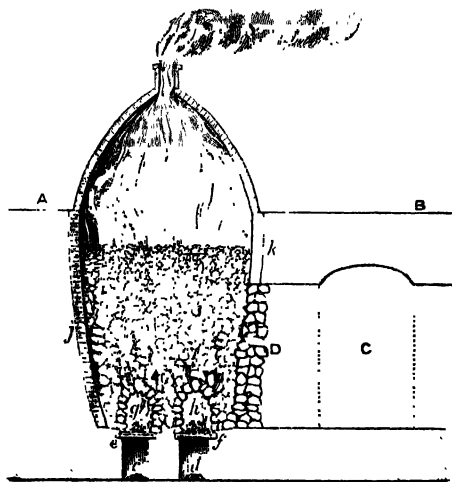


FIG. 366. -Derbyshire limekiln.

Lime is used in coal gas purification, paper making, tanning, as a fertiliser, and in making lime mortar for building purposes, this consisting of a thick paste of slaked lime with three to four times as much sand as quicklime originally taken. Lime made from magnesian limestone slakes slowly and gives a powdery mixture with water; it is called "poor lime," as distinguished from "fat lime," which gives a paste with water. The hardening of mortar consists in the evaporation of the moisture, or its absorption by the bricks, and the slow conversion of the calcium hydroxide into carbonate by atmospheric carbon dioxide; no combination between the lime and the silica of the sand occurs, these substances reacting only above 620° at an appreciable rate (Hüttig and Rosencranz, 1929). Modern mortar usually contains cement in place of lime.

Calcium peroxide is formed as a hydrate, $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, by precipitating lime-water with hydrogen peroxide. From very concentrated solutions at 0° , or in all cases above 40° , anhydrous CaO_2 is precipitated. Calcium peroxide is manufactured for use as an antiseptic by compressing slaked lime and Na_2O_2 , and washing with ice-water. Much free lime is present in it. It is not formed directly from CaO and O_2 (cf. BaO_2). Yellow **calcium tetroxide** CaO_4 , stable at 130° , is formed on warming $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ alone, or better with 30 per cent hydrogen peroxide. It evolves oxygen with dilute

acids : $\text{CaO}_4 + 2\text{HCl} = \text{CaCl}_2 + \text{O}_2 + \text{H}_2\text{O}_3$, and does not liberate iodine from potassium iodide.

Calcium carbonate.—The most abundant mineral of calcium is the carbonate CaCO_3 , which is dimorphous, crystallising in various forms of the hexagonal system as *calcite* (density 2.71) and in the rhombic system as *aragonite* (density 2.92). Calcite is the common form of calcium carbonate ; besides occurring in minerals, it forms the chief constituent of eggshells and bones (together with calcium phosphate), all of which effervesce with acids. Aragonite occurs in the shells of molluses and in coral. In the massive form calcite occurs as *marble*, *limestones* of various kinds, *calc-spar* (a very pure transparent variety of which is Iceland spar) and *chalk*. Chalk consists of the shells of minute marine organisms. A compound of calcium carbonate and magnesium carbonate is *dolomite*, $\text{MgCO}_3 \cdot \text{CaCO}_3$, of which (as well as limestone) whole mountain chains are composed.

Aragonite usually contains strontium and lead carbonates. On passing carbon dioxide into cold lime-water the flocculent amorphous precipitate soon crystallises as calcite ; from hot lime-water aragonite separates. Calcite is the stable form at ordinary temperature and pressure ; it passes into aragonite above 400° .

Bivalent metal carbonates crystallise in the calcite form if the ion radius is 0.78–1.06 Å. and the aragonite form if it is 1.06–1.43 Å. Since the Ca^{++} ion radius is 1.06 Å CaCO_3 can crystallise in both forms. A third form, $\mu\text{-CaCO}_3$, density 2.54, is precipitated from lime-water at 60° (Johnston, 1916). When boiled for a few minutes with cobalt nitrate solution aragonite is coloured lilac but calcite is unchanged (*Meigen's test*) ; an artificial hexagonal form of CaCO_3 called *vaterite* is also coloured.

An unstable hexahydrate $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ (said to occur in pearls and mother-of-pearl), a pentahydrate and perhaps a monohydrate are precipitated by carbon dioxide from lime-water containing sugar (Hume, 1925).

The solubilities in gm./lit. are :

		18°	25°	100°
Calcite	-	0.013	0.0143	0.01779
Aragonite	-	0.015	0.01528	0.01902

At 25° the solubility product is $[\text{Ca}^{++}][\text{CO}_3^{--}] = 7.2 \times 10^{-9}$.

In presence of carbon dioxide about 100 times as much calcium carbonate dissolves (0.94–1.08 gm./lit. at 16° and 1 atm.), calcium bicarbonate $\text{Ca}(\text{HCO}_3)_2$ being formed. A supersaturated solution is formed by passing carbon dioxide rapidly through saturated lime-water.

Flocculent precipitates of Ca, Sr and Ba bicarbonates, decomposing at room temperature, are said to be formed from KHCO_3 and strongly-cooled solutions of the chlorides (Keiser, 1908).

Calcium sulphate occurs as rhombic *anhydrite* CaSO_4 , density 2.94, and more commonly as monoclinic *gypsum* $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, density 2.32, either in transparent crystals of *selenite* (often twinned) or crystalline masses either fibrous (*satín spar*) or opaque (*alabaster*).

Anhydrous calcium sulphate exists in two forms : (a) natural anhydrite and that formed by dehydrating gypsum at a red heat, both practically insoluble ; (b) a soluble form, " setting " with water, produced by dehydrating gypsum at 60°-90° in vacuum over P_2O_5 .

The solubilities of gypsum in gm. $CaSO_4$ per 100 gm. H_2O are :

0°	10	30	40	50	60°
0.176	0.193	0.209	0.210	0.204	0.200

Gypsum can easily be reduced to an extremely fine powder and the solubility increases with the fineness of the grains. This is due to surface-tension forces, which are more pronounced with small particles. The solubility increases with temperature to 40°, and diminishes at higher temperatures.

Gypsum at 120°-130° loses water and forms *plaster of Paris*, the hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$, which when mixed with water evolves heat and quickly solidifies to gypsum, expanding slightly ; it is used for casts. Plaster of Paris at 140° begins to lose water, all of which is rapidly expelled at 200°. The anhydrous $CaSO_4$, density 2.57, rapidly takes up water, but if more strongly heated it hydrates only very slowly (like natural anhydrite) and is said to be " dead-burnt " : its density is 2.96. By heating over 400° slight decomposition into CaO and SO_3 occurs and *estrich plaster* is formed : this sets slowly to a smooth hard surface and is used for floors, walls, etc.

Calcium sulphate hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$ can be obtained in rhombic prisms, density 2.75, by heating for some time on a water bath 20 gm. of gypsum and 50 ml. of conc. HNO_3 : it is a definite compound with a characteristic X-ray spectrum and there is a corresponding selenate, $CaSeO_4 \cdot \frac{1}{2}H_2O$.

Calcium sulphate begins to dissociate at 960° ; when mixed with silica it reacts at 870° and rapidly at 1280° : $CaSO_4 + SiO_2 = CaSiO_3 + SO_3$. Hydrogen chloride decomposes it at a red heat, forming $CaCl_2$.

Precipitated gypsum formed by adding sulphuric acid to a solution of calcium chloride is used as *pearl-hardening* for " filling " glazed paper. Ordinary blackboard " chalk " is made from gypsum.

The double salts $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ (*synygenite*), $CaSO_4 \cdot Na_2SO_4$ (*glauberite*), and $CaSO_4 \cdot 2Na_2SO_4$, are known. Calcium sulphate dissolves in a concentrated solution of ammonium sulphate forming $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$. Strontium and barium sulphates are insoluble.

Calcium sulphite $CaSO_3$ is formed as a white precipitate (solubility 0.24 gm./lit. at 25°) by passing sulphur dioxide into a fairly large volume of lime water, or by mixing solutions of sodium sulphite and calcium chloride. It dissolves in sulphurous acid, forming calcium hydrogen sulphite (bisulphite) $Ca(HSO_3)_2$. This is prepared by passing sulphur dioxide in excess into milk of lime : it is used in sterilising beer casks, and in the manufacture of wood-pulp. Wood consists of *cellulose* and *lignin*, the latter soluble in boiling bisulphite solution. The cellulose is left, and is

used for making paper. On standing exposed to air calcium bisulphite solution deposits crystals of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$.

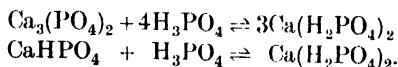
Calcium sulphide CaS is formed as *alkali-waste* in the Leblanc process, or by heating gypsum with charcoal at 900° : $\text{CaSO}_4 + 4\text{C} = \text{CaS} + 4\text{CO}$, or in hydrogen at 600° - 800° . Above 900° , CaS reacts with CaSO_4 : $\text{CaS} + 3\text{CaSO}_4 = 4\text{CaO} + 4\text{SO}_2$. Calcium sulphide is best prepared by passing hydrogen sulphide over gently heated slaked lime: $\text{Ca}(\text{OH})_2 + \text{H}_2\text{S} = \text{CaS} + 2\text{H}_2\text{O}$. It is very sparingly soluble in water, but dissolves when hydrogen sulphide is passed into the suspension, forming calcium hydrosulphide, crystallising as $\text{Ca}(\text{HS})_2 \cdot 6\text{H}_2\text{O}$. The sulphide is hydrolysed by water: $2\text{CaS} + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{Ca}(\text{HS})_2$. Calcium polysulphides CaS_2 to CaS_5 , or possibly CaS_7 , seem to be contained in the reddish-yellow solution (*theion hutor*) made by boiling sulphur with milk of lime. The crystals which separate from concentrated solutions are $\text{CaS}_4 \cdot 3\text{Ca}(\text{OH})_2 \cdot 9\text{H}_2\text{O}$. Calcium thiosulphate $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ is formed by blowing air through a suspension of the sulphide, by cooling a concentrated solution of calcium chloride and sodium thiosulphate, or by heating calcium sulphite and sulphur with water. If the solution is precipitated with sodium carbonate, sodium thiosulphate is formed. $\text{CaS}_2\text{O}_3 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{S}_2\text{O}_3$.

Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ is present in the soil and is used as a fertiliser. It is manufactured by neutralising dilute nitric acid with limestone and evaporating, also by passing oxides of nitrogen into milk of lime or a suspension of calcium carbonate in water until the nitrite in the mixture is decomposed (p. 541). It forms very deliquescent monoclinic crystals $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (two forms, m. pts. 42.7° and 39.7°) soluble in alcohol. According to T. W. Richards the best method of obtaining a pure calcium salt is repeated crystallisation of the nitrate from water or alcohol. The anhydrous salt, m. pt. 561° , dissolves in amyl alcohol. There are also tri- and di-hydrates and a basic nitrate $\text{Ca}(\text{NO}_3)_2 \cdot \text{CaO}$ and hydrates. Calcium nitrate decomposes on heating, leaving calcium oxide.

Calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ occurs in bones and in the mineral *phosphorite*. It is formed as a white amorphous flocculent precipitate on adding ammonium phosphate and a large excess of ammonia to calcium chloride solution: $3\text{Ca}^{++} + 2\text{HPO}_4^{--} + 2\text{OH}' = \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O}$, but the precipitate may be the basic phosphate $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ *hydroxyapatite*. Anhydrous $\text{Ca}_3(\text{PO}_4)_2$, m. pt. 1670° , is shown by the high-temperature phase diagram and X-ray spectrum. Calcium phosphate is nearly insoluble in water, but dissolves in water containing many salts or carbon dioxide, which dissolve the calcium phosphate in the soil and render it capable of absorption by the roots of plants.

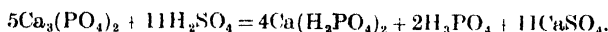
Ordinary sodium phosphate, or better a mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$, precipitates from a calcium salt solution calcium hydrogenc

phosphate CaHPO_4 , either anhydrous or with $4\text{H}_2\text{O}$ according to conditions: $\text{Na}_2\text{HPO}_4 + \text{CaCl}_2 = \text{CaHPO}_4 + 2\text{NaCl}$. This and the normal phosphate dissolve in aqueous phosphoric acid and on spontaneous evaporation the solution deposits crystals of calcium dihydrogen phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2, \text{H}_2\text{O}$:



This is decomposed by water by the reverse of these reactions. It loses water at $100^\circ\text{--}105^\circ$. Pure calcium dihydrogen phosphate (also called **monocalcium phosphate**) is made commercially by dissolving slaked lime or pure limestone in phosphoric acid, crystallising and drying, and is used in American baking powder.

A mixture of the acid phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$, anhydrous calcium sulphate CaSO_4 and phosphoric acid is the fertiliser called *superphosphate of lime*. It is made by macerating ground mineral calcium phosphate (*phosphorite*) with two-thirds of its weight of 70 per cent sulphuric acid:



The reaction is carried out in a horizontal cast-iron cylinder with revolving blades. The mixture issues nearly fluid into pits or *dens*, which are half-filled and then closed. Reaction occurs with rise of temperature and gases (CO_2 , SiF_4 , HF , HCl) escape through a vent to absorption towers. After a day or two the superphosphate is removed, powdered, and carefully dried by hot air in long brickwork chambers.

Apatite (Greek *apatao*, I deceive, since it was confused with many other species) is properly the name of the mineral $3\text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$, but is now applied (with the names *fluorapatite*, *chlorapatite*, etc.) to a group of compounds $3\text{Ca}_3(\text{PO}_4)_2, \text{CaX}$ where X may be F_2 , Cl_2 , $(\text{OH})_2$, CO_3 , SO_4 , etc. The crystals are aggregates of Ca^{++} , PO_4^{--} , and X ions, and apatite should be formulated as $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Related compounds (see p. 360) are *mimetite* (formerly called *mimetisite*) $\text{Pb}_5(\text{PO}_4)_3\text{F}$, *pyromorphite* $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ and *vanadinite* $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$; *wagnerite* is $\text{Mg}_3(\text{PO}_4)_2, \text{MgF}_2$ or $\text{Mg}_2(\text{PO}_4)\text{F}$. **Basic calcium phosphate** $\text{Ca}_4\text{P}_2\text{O}_9$ or $\text{Ca}_3(\text{PO}_4)_2, \text{CaO}$ is a constituent of *basic slag* (p. 920) and it appears on the freezing-point diagram as a definite compound.

Calcium silicates shown in phase diagrams are two forms (α and β) of the **metasilicate** CaSiO_3 (CaO, SiO_2), an **orthosilicate** $\text{Ca}_3\text{Si}_2\text{O}_7$ ($3\text{CaO}, 2\text{SiO}_2$), a **basic metasilicate** $\text{CaSiO}_3, 2\text{CaO}$ or **tricalcium silicate** $3\text{CaO}, \text{SiO}_2$, and three (perhaps four) forms of **orthosilicate** Ca_2SiO_4 ($2\text{CaO}, \text{SiO}_2$). There are also various hydrated forms.

Limestone containing more than 5 per cent of clay on burning forms a lime which gives a *hydraulic mortar* which hardens under water. Vitruvius says the Romans used it for harbour works. In 1796 James Parker prepared *Roman cement* by heating clay and limestone below the sintering point. *Portland cement* (so called because after setting it

resembles Portland stone) is made by heating a mixture of limestone and clay, either mixed with coal as in lime-burning, or by feeding the wet mixture into the top of a revolving inclined tubular furnace, into the lower part of which a blast of air charged with coaldust, which forms an intense flame, is injected (Fig. 367). The materials sinter and the *cement clinker* formed in small nodules is ground to powder.

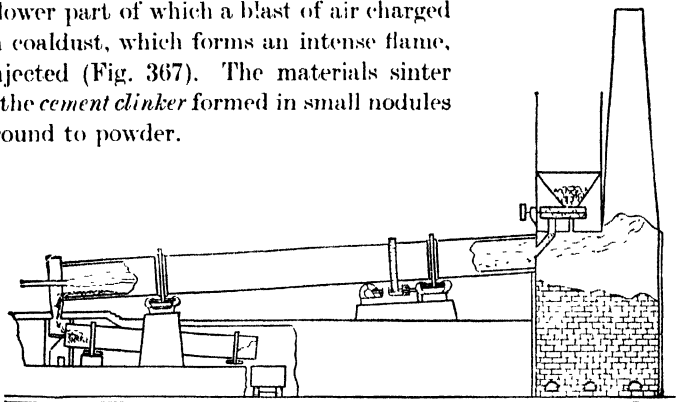
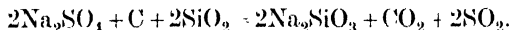


FIG. 367 -- Cement furnace. The upper large tube is the furnace proper, the lower smaller tube, which also revolves, is a cooler.

The constitution and mode of setting of cement are complicated and have been variously explained. Cement clinker contains *tricalcium silicate* $3\text{CaO}\cdot\text{SiO}_2$, *calcium orthosilicate* $2\text{CaO}\cdot\text{SiO}_2$, *tricalcium aluminate* $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, and a *complex calcium aluminate* formerly thought to be $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ but really $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$. Some free lime and calcium aluminoferrite $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ are also present. When mixed with water, cement rapidly hydrates and sets to a gel of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ and adsorbed water. The gel then slowly crystallises. The rapid increase in strength and hardness is mainly due to the partial hydrolysis of the tricalcium silicate to felted needles of calcium hydroxide in a gel of hydrated silicate. Addition of 2.5 per cent of gypsum to the cement clinker before grinding retards the setting.

Glass.—Common *soda glass* contains calcium and sodium silicates and has the *approximate* composition $\text{Na}_2\text{O}\cdot\text{CaO}\cdot 5\text{SiO}_2$. It is made by fusing sand, soda-ash (Na_2CO_3) and limestone, whiting or lime in fire-clay pots or tanks at about 1375°C . or higher. A mixture of saltcake (Na_2SO_4) and charcoal may replace soda-ash but is not much used :



Ordinary glass contains a little aluminium oxide derived from the clay pots. The sand for the best glass must be white and free from iron compounds ; crushed quartz and broken flints are also used.

The green colour due to ferrous silicate may be neutralised by adding manganese dioxide or *pyrolusite* (Greek *pyr* fire, and *luo* I wash) ; this oxidises ferrous to ferric silicate, the yellow colour of which is masked by the purple colour due to manganese. Selenium and cobalt oxide are now used to decolorise bottle glass, and nickel oxide with flint glass.

Bohemian or *potash-glass* contains potassium instead of sodium, has a higher melting point and greater resistance to reagents, and is better adapted for chemical apparatus. *Flint-glass* is potash-glass with lime replaced by lead oxide (PbO). It has a high refractive index and is used for optical purposes but is very soft. *Jena resistance glass* has a low alkali and a higher alumina content (which confers toughness) than ordinary glass, contains barium and zinc oxides, and boron trioxide in place of some silica. Glasses of high softening temperature and resistant to rapid changes of temperature are used for oven ware, laboratory apparatus, etc. They are rich in silica, poor in alkali, and contain boron trioxide, B_2O_3 .

Optical glasses may contain boron trioxide in place of some silica, and barium oxide in place of lime. Two main divisions are recognised: *crown-glass* containing as basic oxide mainly potash or barium oxide, and *flint-glass* containing lead oxide. *Crookes's glass* for spectacles contains rare-earth compounds (praseodymium and neodymium): it allows visible light to pass but absorbs the ultra-violet. A very dark-red glass containing nickel absorbs nearly all visible light but allows some ultra-violet to pass. *Vita-glass*, which transmits some ultra-violet, is nearly free from iron and is made from very pure materials. Ordinary glass absorbs infra-red rays (radiant heat), hence its use for fire-screens.

Coloured glasses are made by adding various substances to the fused glass; in the case of gold the colour develops only after reheating:

Red: gold, selenium, cuprous oxide

Green: chromic oxide, cupric oxide with chromic or ferric oxides and a reducing agent.

Yellow: carbon and sulphates in the melt; cadmium sulphide; sometimes uranium or selenium.

Violet: manganese dioxide.

Blue: cupric oxide, cobalt oxide.

Opaque milky: fluorspar with felspar; cryolite; sometimes tin oxide or calcium phosphate.

Fluorescent greenish-yellow: uranium oxide.

Black: large quantities of ferric oxide and cupric oxide; cobalt, nickel and manganese oxides.

Calcium nitride Ca_3N_2 is a brownish-yellow solid, m. pt. 1195° , formed by passing nitrogen over calcium at 450° or rapidly with fused calcium. It is decomposed by steam: $Ca_3N_2 + 6H_2O = 2NH_3 + 3Ca(OH)_2$. Calcium absorbs ammonia gas, forming $Ca(NH_3)_6$, which on heating forms calcium amide: $Ca(NH_3)_6 = Ca(NH_2)_2 + 4NH_3 + H_2$, and on heating at 400° this gives calcium imide $CaNH$.

Calcium phosphide Ca_3P_2 is formed in red crystals by passing phosphorus vapour over heated calcium or heating calcium phosphate with carbon in the electric furnace (Moissan, 1899). It gives pure phosphine PH_3 with water. The *crude* phosphide, containing Ca_2P_2 and calcium pyrophosphate, is made by passing phosphorus vapour over heated quicklime: $14P + 14CaO = 5Ca_2P_2 + 2Ca_2P_2O_7$; it gives with water spontaneously inflammable phosphine containing P_2H_4 (p. 574).

Calcium carbide CaC_2 was obtained by Wöhler (1862) by heating carbon with an alloy of calcium and zinc. It is manufactured on a large scale by Moissan's process (1894). A mixture of 2 parts of coke and 3 parts of quicklime is heated to over 2000° in an electric furnace : $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$.

The furnace (Fig. 368) is a rectangular tank of fireclay divided into compartments lined with gas-carbon and having a graphite block in the base forming one electrode. The other electrode consists of vertical blocks of carbon suspended from chains and gradually lowered into the furnace as they are consumed. Arcs are struck between the base-plate and these electrodes, and the fused carbide is tapped, cooled, and broken into pieces in a jaw-crusher. The commercial carbide is greyish-black. According to Moissan (1903) the pure carbide is formed in colourless transparent

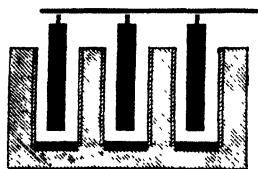


FIG. 368.— Calcium carbide furnace.

crystals by heating calcium hydride in acetylene and the product in vacuum, but this is doubtful (Botolfsen, 1922).

Calcium carbide is decomposed by water to give acetylene : $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$; 1 kg. of commercial carbide usually gives about 300 litres of gas.

Calcium carbide is an energetic reducing agent. A powdered mixture with ferric oxide and ferric chloride burns violently when kindled with a taper, and fused metallic iron is produced.

Calcium oxalate CaC_2O_4 is formed as a white precipitate, insoluble in acetic acid but soluble in dilute hydrochloric acid, when ammonium oxalate solution is added to a solution of a calcium salt, preferably after adding ammonium chloride and ammonia. On heating at 560° for 1 hour it gives the carbonate : $\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}$, or at a red heat the oxide CaO . These reactions are used in the gravimetric estimation of calcium ; in the volumetric method the precipitate of oxalate is washed, decomposed with warm dilute sulphuric acid, and the oxalic acid is titrated at 60° with permanganate : $2\text{KMnO}_4 + 5\text{CaC}_2\text{O}_4 + 8\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 5\text{CaSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$. Calcium oxalate occurs in small crystals (*raphides*) in some plants.

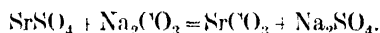
STRONTIUM

History.—A peculiar mineral found in the lead mine of Strontian in Argyllshire was examined by Crawford and Cruickshank in 1790, and later by Hope, Kirwan and Klaproth. They found it to contain a new "earth" which Hope called *strontites* and Klaproth *strontia*. The mineral is *strontianite* or strontium carbonate SrCO_3 . Another mineral is strontium sulphate or *celestine* SrSO_4 , so called from the pale-blue colour of some specimens. The element strontium occurs practically only in these two rather uncommon minerals. Metallic strontium was discovered by Davy in 1808.

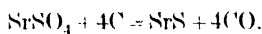
Strontium and its compounds.—Metallic strontium is prepared by the electrolysis of the fused chloride, by heating the oxide with aluminium, and by preparing strontium amalgam by electrolysis with a mercury cathode and driving off the mercury at a high temperature in hydrogen (when the hydride is first formed and then decomposes). It is a silver-white soft metal which oxidises very easily in air, burns in oxygen, and decomposes water.

Strontium hydride SrH_2 is formed by strongly heating the metal in hydrogen and is a white solid resembling calcium hydride in its properties.

Strontium chloride $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ is a colourless crystalline salt, efflorescent in air (it is much less soluble in water than calcium chloride). It is prepared by dissolving native strontium carbonate in hydrochloric acid, oxidising any iron with chlorine and digesting with some strontium carbonate precipitated from some of the solution by sodium carbonate, when ferric oxide is precipitated: the liquid is filtered, evaporated and crystallised. It may also be prepared from the native sulphate by fusing with sodium carbonate, when strontium carbonate is formed, which is washed with water and dissolved in hydrochloric acid:

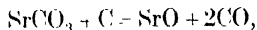


The sulphate may also be heated with carbon when strontium sulphide is formed, which is dissolved in hydrochloric acid:

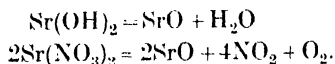


Anhydrous strontium chloride is only sparingly soluble in absolute alcohol; calcium chloride is readily soluble, whilst barium chloride is practically insoluble in ethyl alcohol but dissolves in methyl alcohol. (The bromides and iodides of strontium and barium are readily soluble in alcohol.)

Strontium oxide (*strontia*) SrO is obtained by strongly heating the carbonate, more readily when mixed with carbon:



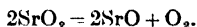
or at a red heat from the hydroxide and nitrate:



It is a white mass which combines with water with evolution of heat to form **strontium hydroxide** $\text{Sr}(\text{OH})_2$. This forms a readily soluble crystalline hydrate $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, which effloresces to a hydrate with $1\text{H}_2\text{O}$, and at 100° this gives $\text{Sr}(\text{OH})_2$. Like calcium hydroxide and unlike barium peroxide, strontium hydroxide forms the oxide at a dull-red heat. The hydroxide is used in sugar refining, since it forms a sparingly soluble compound $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ with cane sugar, which can so be separated from the molasses.

Strontium peroxide SrO_2 is formed at a dull-red heat from the oxide and oxygen but only *under pressure* (125 kg./sq. cm.). It is similar to barium peroxide. A crystalline hydrate $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ is precipitated in pearly scales

on adding hydrogen peroxide to a solution of strontium hydroxide ; on heating gently it gives SrO_2 which decomposes at a higher temperature :



Strontium carbonate is precipitated from a solution of a strontium salt by sodium carbonate ; it is sparingly soluble (0.01 gm./lit. at 15°) but dissolves in water containing carbonic acid to form a bicarbonate. It is decomposed at a higher temperature than calcium carbonate (1 atm. pressure of CO_2 at 1258°).

Strontium nitride Sr_3N_2 is formed by heating the metal in nitrogen. It is black and is readily decomposed by water, evolving ammonia.

Strontium nitrate $\text{Sr}(\text{NO}_3)_2$, crystallising anhydrous from hot concentrated solutions, is prepared by dissolving the carbonate in dilute nitric acid ; it is used mixed with sulphur and charcoal to make " crimson fire " for fireworks. It is insoluble in alcohol and amyl alcohol and less soluble in water than calcium nitrate. Strontium nitrate at the m. pt. (645°) gives mostly strontium nitrite $\text{Sr}(\text{NO}_2)_2$ (cf. barium nitrate). Strontium nitrate is freed from barium by adding calcium sulphate solution (which precipitates barium sulphate), filtering and crystallising.

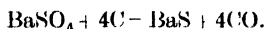
Strontium sulphate SrSO_4 is sparingly soluble in water (0.1 gm. per lit. at 15°) but soluble in dilute hydrochloric acid ; it is insoluble in ammonium sulphate solution, but is more soluble in strontium nitrate solution than in water. Unlike calcium sulphate it does not form a hydrate. It is less soluble than calcium sulphate and a saturated solution of calcium sulphate gives a precipitate with a strontium salt.

Strontium phosphate $\text{Sr}_3(\text{PO}_4)_2$ is an amorphous solid precipitated from neutral solution by Na_3PO_4 . The precipitate of SrHPO_4 formed with Na_2HPO_4 is at first amorphous, but then crystallises. On heating it forms $\text{Sr}_2\text{P}_2\text{O}_7$, the pyrophosphate, and the metaphosphate $\text{Sr}(\text{PO}_3)_2$, is also known.

Strontium salts impart a splendid crimson colour to the Bunsen flame, and it is interesting that the spectrum of the flame (that of crimson fire in a theatre) had been examined by Fox Talbot in 1826 long before Bunsen and Kirchhoff invented spectrum analysis.

BARIUM

History.—The heavy mineral " heavy spar " (density 4.5) is found associated with metallic ores such as galena ; it is barium sulphate BaSO_4 . Early in the seventeenth century* a shoemaker of Bologna found that when strongly heated with charcoal this stone produces a material (barium sulphide) which is phosphorescent after exposure to light.



Scheele in 1774 showed that heavy spar is the sulphate of an " earth "

* According to Licetus, *Lithosphorus, sive de Lapide Bononiensi*, 1640, p. 12, the discovery was made in 1602 by Vincent Casciorolo.

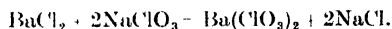
which was called *barote* (Greek, *barys* - heavy) by Guyton de Morveau and *barytes* by Kirwan. Metallic barium was obtained by Davy in 1808 from the amalgam formed by electrolysis.

Occurrence.—Barium occurs as *barytes* or *heavy spar*, the sulphate BaSO_4 ; as *witherite*, the carbonate BaCO_3 (isomorphous with aragonite and a common gangue material in lead mines); as *alstonite* $\text{BaCO}_3, \text{CaCO}_3$ in rhombic crystals and in monoclinic crystals as *barytocalcite*. Barium also occurs as an impurity in some other ores, e.g. of manganese (*psilomelane*, see p. 899).

Barium and its compounds.—Metallic barium is prepared by processes analogous to those used for strontium; very pure barium is obtained by the slow distillation of the dry amalgam (obtained by electrolysis with a mercury cathode), when mercury first distils and then barium. It is a silver-white soft metal which inflames spontaneously in air and decomposes water and alcohol. Barium hydride BaH_2 is formed from the elements at a bright red heat.

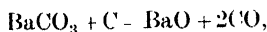
Barium chloride BaCl_2 is prepared from the native carbonate and sulphate by methods analogous to those used for strontium chloride. A large excess of sodium carbonate must be used in decomposing the barium sulphate, and a high temperature in its reduction with carbon. Barium chloride crystallises as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and the crystals are neither efflorescent nor deliquescent. It is readily soluble in water but insoluble in absolute alcohol, and it is almost insoluble in concentrated hydrochloric acid, which precipitates it from solution.

Barium chlorate $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ is used in the preparation of chloric acid (p. 273) and is made by evaporating a solution of sodium chlorate and barium chloride, when sodium chloride is deposited:

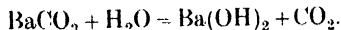


The solution is filtered through a hot-water funnel and further evaporated, when the barium chlorate crystallises on cooling. It is purified by recrystallisation.

Barium oxide (*baryta*) BaO is best obtained by heating the nitrate strongly (to decompose any peroxide formed), or the iodate (when a periodate is first formed). Barium carbonate is only slightly decomposed even at a bright-red heat (it attacks platinum at a red heat) unless mixed with charcoal:



or heated in a current of steam, when the hydroxide is formed:



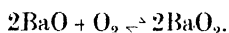
The dissociation pressures ($\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$) of barium carbonate are:

$t^\circ \text{C.}$	-	-	915	1020	1120	1220	1300	c. 1352
$p \text{ mm.}$	-	-	0.4	4.3	24.4	114	381	760

Barium oxide combines vigorously with water with evolution of heat to form barium hydroxide $\text{Ba}(\text{OH})_2$; this gives a crystalline hydrate

$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, very soluble in hot water. On exposure to air free from carbon dioxide the crystals effloresce to $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, and at 100° $\text{Ba}(\text{OH})_2$ is formed. This fuses on heating and (unlike calcium and strontium hydroxides) does not lose water completely even at a high temperature. A solution of barium hydroxide in water (*baryta water*) gives a white precipitate of barium carbonate with carbon dioxide, soluble in excess to form a bicarbonate decomposed on boiling. Barium hydroxide is a strong base and may be used in volumetric analysis instead of sodium hydroxide, since any carbonate formed on exposure to air is precipitated and does not remain in solution to interfere with the colour-changes of some indicators. Baryta forms a sparingly soluble compound with cane sugar, but is not used in sugar refining since barium salts are poisonous.

Barium peroxide BaO_2 is readily formed by passing oxygen or air free from carbon dioxide over barium oxide at a dull red-heat; at a bright-red heat it decomposes into oxygen and barium oxide:



The dissociation pressures at different temperatures are:

555°	650°	720°	790	795° C.
25	65	210	670	760 mm.

A crystalline hydrate $\text{BaO}_2 \cdot 5\text{H}_2\text{O}$ is formed by adding hydrogen peroxide to baryta water, and when gently heated it forms the anhydrous peroxide. By adding baryta water to hydrogen peroxide the compounds $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ (yellow) and $\text{BaO}_2 \cdot 2\text{H}_2\text{O}_2$ are precipitated.

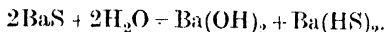
Barium carbonate BaCO_3 is formed as a white precipitate on adding an alkali carbonate to a solution of barium chloride. It is more soluble (0.02 gm. per lit.) than strontium carbonate (0.01 gm. per lit.) and is slightly hydrolysed in solution; a suspension of barium carbonate is sometimes used in qualitative group separation as it precipitates ferric, chromic and aluminium hydroxides from solutions of their salts, but not zinc or manganese salts. Barium carbonate is stable at a high temperature, and can be heated with a blowpipe without much change; it attacks platinum at a red heat. It dissolves in water containing dissolved carbon dioxide to form a solution of the bicarbonate $\text{Ba}(\text{HCO}_3)_2$.

Barium nitride Ba_3N_2 is a black solid formed by heating barium in nitrogen; it evolves ammonia with water.

Barium nitrate $\text{Ba}(\text{NO}_3)_2$, which crystallises anhydrous, is made by dissolving the carbonate in dilute nitric acid and evaporating. It is much less soluble in water than strontium nitrate and is insoluble in alcohol and in nitric acid (which precipitates it from solution). A pure barium compound is best obtained by repeated crystallisation of the nitrate; from the pure nitrate the carbonate is precipitated with ammonium carbonate and is then dissolved in an acid to form the corresponding salt. Barium nitrate mixed with charcoal and sulphur forms "green fire" in pyrotechny; barium salts give an apple-green flame when heated on platinum wire in the Bunsen flame.

Barium nitrite $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ is prepared by mixing hot nearly saturated solutions of sodium nitrite and barium chloride, filtering from the sodium chloride with a hot-water funnel, and allowing to crystallise. The salt is recrystallised from water and dried over sulphuric acid. It is very soluble.

Barium sulphide BaS is obtained by reducing the sulphate with carbon (see above), but most conveniently by the action of hydrogen sulphide on gently heated $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$; it is easily soluble and is hydrolysed:



Polysulphides of barium and strontium are known.

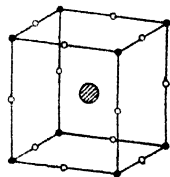
Barium sulphate BaSO_4 is formed by adding dilute sulphuric acid or a solution of a sulphate to a solution of a barium salt, as a fine white precipitate nearly insoluble in water (2.4 mgm. per litre) and acids, except hot concentrated sulphuric acid which forms the acid sulphate $\text{Ba}(\text{HSO}_4)_2$, or in hot very concentrated hydrochloric acid. Precipitated barium sulphate is used as a pigment (*blanc fixe* or *permanent white*), but has a poor covering power. *Lithopone* is a mixture of barium sulphate and zinc sulphide and oxide made by precipitation:



and heating the precipitate. It has a good covering power, and does not darken on exposure to hydrogen sulphide, but darkens on exposure to light.

Barium sulphate carries down from solution various soluble salts, especially potassium sulphate and sulphates, salts of trivalent metals (Fe, Cr), nitrates, and chlorates, which cannot be removed by washing. It also adsorbs barium chloride and is slightly soluble in dilute hydrochloric acid and in many salt solutions. Barium sulphate is only slightly decomposed at a white heat. These properties are of importance in quantitative analysis. Barium and strontium sulphates are converted into carbonates by boiling with alkali carbonate, and the reaction is reversible. Barium sulphate is almost quantitatively converted to carbonate on fusion with 8-9 mols. of potassium carbonate, but barium carbonate is only very incompletely converted into sulphate on fusion with potassium sulphate.

Barium titanate BaTiO_3 , formed by heating barium oxide and titanium dioxide TiO_2 , is interesting in having an extraordinarily high dielectric constant, so that it is called a *ferroelectric substance*, by analogy with ferromagnetic iron. It has also a ferroelectric Curie point (analogous to the magnetic Curie point of iron at 760). The crystal lattice is that of the mineral *perovskite* CaTiO_3 , and this occurs also with BaZrO_3 , NaNbO_3 , LaGaO_3 , LaAlO_3 , LaFeO_3 , KIO_3 , and KNiF_3 . The ideal perovskite type lattice ABO_3 is cubic with an A atom (Ca, Ba, etc.) at the centre, B atoms (Ti etc.) at the eight corners, and oxygen atoms on the twelve edges, so that the unit cell has the composition $\text{A} + \frac{1}{8}(8\text{B}) + \frac{1}{4}(12\text{O}) = \text{ABO}_3$. In the extended lattice, each



⊙ = Ba ○ = O ● = Ti

Ti at a corner is surrounded by six oxygens, forming TiO_6 octahedra. A similar arrangement, but without a central atom in the cube, is found with rhenium trioxide ReO_3 .

The atomic weights of magnesium, calcium, strontium and barium have been determined by precipitating the chlorides or bromides with silver nitrate. The valencies follow from the atomic heats of the metals.

CHAPTER XXXIX

MAGNESIUM, ZINC, CADMIUM AND MERCURY

It has been stated (p. 751) that the metals of Group II are divided into an **even series** containing beryllium, magnesium, calcium, strontium, and barium, and an **odd series** containing zinc, cadmium, and mercury. Since beryllium and magnesium are more like zinc than the alkaline earth metals, they are considered in the present chapter.

The physical properties of the metals of the **odd series** in Group II are :

	Zn	Cd	Hg
Atomic number - - -	30	48	80
Electron configuration -	2·8 18·2	2 8 18 18·2	2·8·18·32·18·2
Density - - - -	7·1	8·64	13·5955(0°)
Atomic volume - - -	9·21	13 01	14·02
Melting point - - -	419·4°	320·9°	38·90°
Boiling point - - -	920	767·3°	356·95°

The two parts of Group II are much more alike than those of Group I although they differ more than the odd and even series of Groups III and IV, where there is very little difference between the series in a group. Beryllium and magnesium in some ways resemble the elements of the odd series, with which they are often classified, and beryllium shows many analogies not only with magnesium but also aluminium in Group III : beryllium hydroxide is precipitated by ammonia and dissolves in sodium hydroxide solution, and beryllium salts are hydrolysed. This divergence from group properties is probably connected with the small size of the Be^{++} ion : the ions Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++} form increasingly strong basic oxides.

The normal valency in the sub-group (probably also in the mercurous compounds Hg_2X_2) is two.

All the elements form basic oxides MO (mercury also forms the basic oxide Hg_2O) and, except mercury, basic hydroxides $\text{M}(\text{OH})_2$, those of Be and Mg and of the odd series elements being very sparingly soluble. Cadmium oxide is brown, mercurous oxide black and mercuric oxide yellow or red ; the other oxides are white but zinc oxide is yellow when hot. Unstable hydrated peroxides (but not of beryllium) are formed only indirectly, *e.g.* by the action of hydrogen peroxide on the oxides or hydroxides.

The metals are all silver-white. Beryllium, magnesium, zinc and cadmium crystallise in close-packed hexagonal, mercury in rhombohedral, lattices (the alkaline earth metals crystallise in cubic lattices).

Magnesium and zinc oxidise only slowly at room temperature in air; beryllium, cadmium and mercury are stable in air. Magnesium powder decomposes hot water slowly, and zinc and cadmium decompose steam on heating.

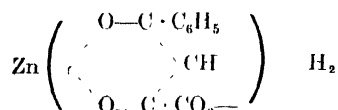
Beryllium and magnesium resemble the elements of the odd series in forming soluble *sulphates*, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (isomorphous with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), and double sulphates, $\text{K}_2\text{Be}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (isomorphous with $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$), and in forming organometallic compounds $\text{Be}(\text{CH}_3)_2$ and $\text{Mg}(\text{CH}_3)_2$, etc., similar to $\text{Zn}(\text{CH}_3)_2$, $\text{Cd}(\text{CH}_3)_2$, $\text{Hg}(\text{CH}_3)_2$, etc.

The sulphides of beryllium, magnesium, and the alkaline earth metals are not precipitated from solution by hydrogen sulphide: those of zinc, cadmium and mercury are, and decrease in solubility in this order. The sulphides of Be, Mg, Ca, Sr and Ba are hydrolysed by water: ZnS is soluble in dilute and CdS in concentrated hydrochloric acid, whilst HgS is insoluble even in boiling nitric acid but dissolves in hot aqua regia.

Zinc, cadmium and mercury are sometimes classed as *transitional elements* (p. 370), since the cations have 18-electron shells, although they are uniformly bivalent. They show an increasing tendency to form covalent compounds from zinc to mercury, fused zinc chloride being a conductor but mercuric halides almost non-ionised. Mercury is peculiar in forming the two series of *mercurous* and *mercuric* compounds, with entirely different reactions. The mercurous compounds closely resemble those of silver or univalent copper: the mercuric are analogous to compounds of bivalent copper, zinc and cadmium.

Beryllium, magnesium, zinc, cadmium and mercury do not give distinctive flame colorations.

Zinc shows a covalency of 4 with a tetrahedral arrangement of valencies in the optically active derivatives of benzoylpyruvic acid:



and zinc and cadmium show a covalency of 6 with an octahedral arrangement of valencies in the optically active compounds with ethylenediamine [Zn en_3] Cl_2 and [Cd en_3] Cl_2 (See page 425).

BERYLLIUM

Vauquelin in 1798 found that the mineral *beryl* (Fig. 369) contains a peculiar earth, differing from lime and alumina by forming a soluble sulphate which does not produce alums. The true or Peruvian *emerald* (cf. p. 809) is a transparent variety of beryl, coloured green by oxide of chromium. *Aquamarine* is a bluish-green variety. The formula of beryl is $3\text{BeO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$.

To prepare beryllium salts from beryl, it is fused with potassium carbonate, the melt evaporated with sulphuric acid, and digested with water. Silica is filtered off, and on cooling the evaporated filtrate nearly all the aluminium separates in the form of potash alum. The mother liquor is then poured into a concentrated solution of ammonium carbonate and allowed to stand. **Beryllium hydroxide** $\text{Be}(\text{OH})_2$ and **carbonate** BeCO_3 , are soluble in ammonium carbonate, whilst ferric hydroxide and alumina are precipitated. The filtrate on boiling deposits a basic beryllium carbonate. If this is ignited **beryllium oxide** BeO remains as a white powder soluble in hot concentrated sulphuric acid; the solution on cooling deposits crystals of **beryllium sulphate** $\text{BeSO}_4, 4\text{H}_2\text{O}$, with a sweet taste (hence the name *glucinum* formerly given to the element). The sulphate does not form mixed crystals with CuSO_4 , FeSO_4 , etc., and thus differs from ZnSO_4 and MgSO_4 .

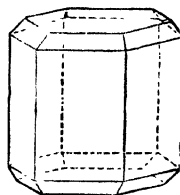


FIG. 369.—Crystal of beryl.

By passing chlorine over a heated mixture of the oxide and carbon **beryllium chloride** BeCl_2 sublimes in white crystals which fume in moist air. The vapour density of the chloride (b. pt. 520°) corresponds above 630° with the formula BeCl_2 . Metallic **beryllium** is obtained by the electrolysis of a fused mixture of the chloride with sodium and ammonium chlorides, or of the fluoride with sodium fluoride in a nickel crucible with a carbon anode. It is a hard white metal, density 1.812, m. pt. 1280°, burning brilliantly in air when heated in the form of powder, but it does not decompose steam even at a red heat. It is readily soluble in hydrochloric acid and in dilute sulphuric acid, but not in nitric acid, and readily soluble in alkalis (cf. aluminium). Beryllium is a constituent of some alloys.

Beryllium hydroxide $\text{Be}(\text{OH})_2$ is soluble in alkalis but is reprecipitated on boiling the solution. It is readily soluble in ammonium carbonate and a basic carbonate is precipitated on boiling the solution or passing a rapid current of steam through it. By these reactions it is distinguished from alumina, which it otherwise closely resembles. **Beryllium nitrate** $\text{Be}(\text{NO}_3)_2$ is used in making gas mantles, a small quantity being added to the thorium and cerium nitrates (p. 846).

On evaporating beryllium hydroxide with acetic acid a characteristic **basic acetate** $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ is formed. This is readily volatile (b. pt. 330°), giving the normal vapour density and is soluble in chloroform. The X-ray examination of the crystalline compound shows that the four beryllium atoms are arranged at the corners of a regular tetrahedron, with the oxygen at the centre, and the six edges are occupied by the acetate groups.

MAGNESIUM

History.—In 1695 Nehemiah Grew obtained from the water of a mineral spring at Epsom a peculiar salt which was called *Epsom salt*, which is **magnesium sulphate** $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; **magnesium chloride** MgCl_2 is contained in sea water. Magnesium and calcium compounds were distinguished by Hoffmann in 1722. By precipitating solutions of these salts with potassium or sodium carbonate, a basic carbonate called *magnesia alba* is obtained. Black in 1754 showed that this contains fixed air or carbon dioxide combined with *calcined magnesia* or **magnesium oxide** MgO , left after ignition of *magnesia alba*. Metallic magnesium was obtained in an impure state by Davy in 1808, and the coherent metal by Bussy in 1829 by fusing the anhydrous chloride with potassium.

Occurrence.—Magnesium is widely distributed, occurring as *magnesite* MgCO_3 , *dolomite* $\text{MgCO}_3 \cdot \text{CaCO}_3$, *kieserite* $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, *kainite* $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and *carnallite* $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. It is also contained in *spinel* MgAl_2O_4 and *olivine* Mg_2SiO_4 ; *talc* and *meerschaum* are hydrated silicates, *asbestos* is calcium magnesium silicate, and other common rock-forming minerals containing magnesium silicate are *augite* and *serpentine*. All plants and animal tissues contain small amounts of magnesium: it is contained in *chlorophyll*, the green colouring-matter of plants.

Magnesium.—Metallic magnesium is prepared by the electrolysis of fused magnesium chloride or the fused magnesium chloride and potassium chloride obtained by heating carnallite. The cathode is the iron crucible, the anode is of carbon enclosed in a porcelain tube. The chlorine is led off and the metal floats to the surface, being protected by a current of hydrogen or coal gas. The electrolysis of magnesium oxide dissolved in molten magnesium fluoride, and the reduction of the oxide by carbon at 2000° have also been used. The semi-fused metal is pressed into wire, which is then rolled into ribbon.

Magnesium is silver-white, soft, and very light. It is stable in dry air but soon becomes covered with oxide in moist air. It burns with an intense white light when heated in air, producing the oxide MgO and a little nitride Mg_3N_2 . It also continues to burn in sulphur vapour, steam, carbon dioxide, sulphur dioxide, nitric oxide and nitrogen dioxide; it reduces carbon monoxide when heated. Magnesium reduces sodium and potassium oxides on heating. Magnesium powder mixed with powdered potassium chlorate or barium peroxide burns explosively when kindled, producing a blinding white flash; the mixture is used in photography and for signalling and star-shells. A mixture of magnesium and dry amorphous silica may also be used.

Although the metal has a high boiling point, fine crystals are obtained by sublimation in a vacuum tube below 600° . It is a very light metal and is a constituent of light alloys. Magnesium is used as a "getter" in radio-

valves to remove the last trace of gas from the bulb : the metal is put on the filament and volatilised by heat, condensing as a bright mirror on the glass. (Phosphorus is also used as a "getter.")

Magnesium dissolves readily in dilute acids, but not in alkalis. Magnesium powder decomposes hot water and the amalgam decomposes cold water. It precipitates silver, copper, lead and mercury from solutions of their salts, but reaction is rarely quantitative, some basic salt being precipitated and hydrogen evolved.

MAGNESIUM COMPOUNDS

Unlike calcium, barium and strontium, but like zinc, cadmium and mercury, magnesium does not form a hydride directly. Magnesium fluoride MgF_2 is sparingly soluble ; it crystallises in the tetragonal system, all the other halides being hexagonal.

Magnesium chloride $MgCl_2$ is very soluble. It is usually prepared from *carrollite* $KCl, MgCl_2, 6H_2O$ which occurs in large quantities in the Stassfurt deposits. It fuses at 176° , undergoing decomposition with deposition of practically all the potassium chloride, and fused magnesium chloride $MgCl_2, 6H_2O$ remains, which crystallises on cooling. The crystals are very deliquescent and are used in lubricating cotton thread in spinning. Magnesium chloride forms hydrates with 12, 8, 6, 4 and $2H_2O$. Magnesium salts are very little hydrolysed in solution, since magnesia is a strong base, but if the crystalline hydrates of magnesium chloride are heated they undergo hydrolysis ; hydrochloric acid and steam are evolved and magnesium oxychloride Mg_2OCl_2 is left, and on strongly heating in air this evolves *chlorine* and leaves the oxide : $2Mg_2OCl_2 + O_2 = 4MgO + 2Cl_2$. Anhydrous magnesium chloride is prepared by heating the hexahydrate in a vacuum or in a current of hydrogen chloride. Another method is to add ammonium chloride to the solution, evaporate, and heat. The double salt $MgCl_2, NH_4Cl, 6H_2O$ which is left on evaporation loses water and the residual $MgCl_2, NH_4Cl$ when strongly heated evolves hydrogen chloride and ammonia, leaving fused anhydrous magnesium chloride.

If a concentrated solution of magnesium chloride is mixed with magnesium oxide, the paste solidifies to a hard white mass of a hydrated magnesium oxychloride $MgCl_2, 5MgO$, used as a dental stopping and as a finish for plaster, since it takes a fine polish.

Magnesium bromide $MgBr_2, 6H_2O$ and magnesium iodide $MgI_2, 8H_2O$ occur in some mineral springs and are prepared in the same way as the chloride, by dissolving magnesium oxide or carbonate in the acids.

Magnesium oxide MgO occurs in octahedral crystals as the mineral *periclase*. It is formed as a white powder by burning the metal in air or

oxygen, and by heating the hydroxide, nitrate, basic carbonate or native carbonate (*magnesite*). When prepared by heating the carbonate, it is called *calcined magnesia*. Two varieties are formed, light and heavy, with densities in the ratio 1 : 3.5, from the corresponding carbonates. Magnesium oxide is only very sparingly soluble, but it slowly combines with water, forming the hydroxide, and it turns moist red litmus paper blue. It fuses only at a very high temperature and is used for refractory bricks for furnaces. It is reduced by carbon in the electric furnace, forming magnesium carbide. A crystalline oxide is produced by heating the powder strongly in a current of hydrogen chloride.

Magnesium hydroxide $\text{Mg}(\text{OH})_2$ occurs crystalline as the mineral *brucite*. It is prepared by precipitating a solution of magnesium sulphate or chloride with alkali hydroxide; the white precipitate (insoluble in excess of alkali) is washed and dried at 100° . On the large scale it is made by precipitating a solution of magnesium chloride with milk of lime.

The solubility of magnesium hydroxide (0.01 gm. per litre of water at 18°) is reduced by addition of potassium or sodium hydroxide, but increased by the addition of ammonia and especially of ammonium chloride. This reaction is applied in qualitative analysis, where magnesium is kept in solution by ammonium chloride whilst the metals of the groups III, IV, and V are precipitated by NH_4OH , NH_4HS , and $(\text{NH}_4)_2\text{CO}_3$, respectively.

The solubility in ammonium salts may be explained as follows. If an ammonium salt is brought in contact with $\text{Mg}(\text{OH})_2$ the OH' ions of the latter are withdrawn to form practically un-ionised NH_4OH , the ionisation of which is still further reduced by the excess of NH_4^+ ions of the NH_4Cl . More $\text{Mg}(\text{OH})_2$ therefore dissolves to provide a further supply of OH' ions, and the process goes on until the solubility product $[\text{Mg}''] \times [\text{OH}']^2$ is reached, or if this cannot be attained, until all the $\text{Mg}(\text{OH})_2$ is dissolved.

Magnesium peroxide, probably MgO_2 , is obtained in an impure state by precipitating a solution of the sulphate mixed with hydrogen peroxide with sodium hydroxide. After drying it is used as an antiseptic in tooth-pastes, etc.

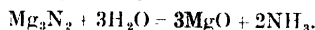
The normal **magnesium carbonate** MgCO_3 occurs native as *magnesite* in large amounts in Greece and in other places; the hydrate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ is the rare mineral *nesquehonite*. This also slowly crystallises from a solution of 20 gm. of Epsom salt and 14 gm. of sodium bicarbonate in 150 ml. of water. The precipitates formed by adding alkali carbonates to solutions of magnesium salts are always **basic carbonates**. From solutions at the ordinary temperature, the precipitate after drying is a light loose powder—*magnesia alba levis*. From a boiling saturated solution a denser crystalline precipitate is thrown down; this is evaporated to dryness, washed, and dried at 100° , and is known as

magnesia alba ponderosa. Both are used in medicine, and have approximately the formulæ $MgCO_3$, $Mg(OH)_2$ with $3\frac{1}{2}$ and $3H_2O$, respectively. Magnesium carbonate is much more easily decomposed by heat than calcium carbonate :

$$MgCO_3 = MgO + CO_2.$$

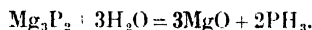
If the powdered carbonate or basic salts are suspended in water and a current of carbon dioxide is passed in, they dissolve readily, producing a solution of magnesium bicarbonate $Mg(HCO_3)_2$, known as *fluid magnesia*. The basic carbonate is precipitated from it on boiling.

Magnesium nitride Mg_3N_2 is a yellow solid obtained by strongly heating magnesium in a stainless steel boat in nitrogen or at a lower temperature in ammonia gas. It is decomposed by water :



Magnesium nitrate is formed as deliquescent crystals $Mg(NO_3)_2 \cdot 6H_2O$ by evaporating a solution of the oxide or carbonate in dilute nitric acid. It is soluble in alcohol.

Magnesium phosphide Mg_3P_2 is obtained by heating magnesium and phosphorus ; it is decomposed by water with evolution of phosphine :



This is used as a test for phosphates ; the solid is heated with magnesium powder in an ignition tube, when magnesium phosphide is formed, and on breathing on the cooled residue a smell of phosphine is noticed.

Tertiary magnesium phosphate $Mg_3(PO_4)_2$ occurs in bones and in the seeds of cereals, and is precipitated from a solution of 20 gm. of Epsom salt in a litre of water by a solution of 19.4 gm. of $Na_2HPO_4 \cdot 12H_2O$ and 4 gm. of $NaHCO_3$ in a litre of water. Ordinary sodium phosphate Na_2HPO_4 slowly precipitates **magnesium hydrogen phosphate** $MgHPO_4 \cdot 3H_2O$, slightly soluble in cold water. The **acid phosphate** $Mg(H_2PO_4)_2 \cdot 2H_2O$ is formed by dissolving magnesium oxide in hot concentrated phosphoric acid. If a solution of a magnesium salt is mixed with solutions of ammonium chloride and ammonia and a phosphate added, a crystalline precipitate is deposited, slowly from dilute solutions but more rapidly on stirring or scratching the sides of the beaker with a glass rod, or shaking in a stoppered bottle. This is **magnesium ammonium phosphate** $Mg(NH_4)PO_4 \cdot 6H_2O$, sparingly soluble in water (0.07 gm./lit. at 15°) and less so in dilute ammonia (0.023 gm./lit. at 15° in equal vols. 0.880 ammonia and water) ; its formation is a test for a phosphate or magnesium. On heating to dull redness it is converted into **magnesium pyrophosphate** $Mg_2P_2O_7$, in which form magnesium is estimated in gravimetric analysis :



Magnesium ammonium phosphate occurs in some urinary calculi.

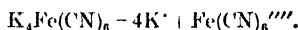
Magnesium sulphide MgS is formed by direct combination of the elements; it is hydrolysed by water so that alkali sulphides precipitate only the hydroxide, but a solution probably containing **magnesium hydrosulphide** $\text{Mg}(\text{HS})_2$ is formed by passing hydrogen sulphide into a suspension of the oxide in water. It decomposes on warming, evolving *pure* hydrogen sulphide.

Magnesium sulphate occurs native as *kieserite* $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, practically insoluble in cold water but soluble on boiling; the heptahydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ separates on cooling in colourless crystals of *Epsom salt*.

Epsom salt is made by dissolving magnesite (native $\text{Mg}(\text{CO}_3)$) or dolomite (native $\text{Mg}(\text{CO}_3, \text{CaCO}_3)$) in boiling dilute sulphuric acid and filtering from calcium sulphate. Iron is separated by boiling with a little precipitated magnesium carbonate, and the filtrate on evaporation and cooling yields crystals of Epsom salt. Magnesium sulphate is used as a purgative, as a dressing for cotton goods, and in dyeing with aniline colours.

Hydrates of MgSO_4 are known with 7 (2 forms), 6, 5, 4, 2 (?), $1\frac{1}{2}$, $1\frac{1}{4}$ and $1\text{H}_2\text{O}$; at 150° *kieserite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) is formed from Epsom salt, and from *kieserite* at 200° the anhydrous sulphate. The common hydrate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is isomorphous with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, but a monoclinic variety, isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is known. When very strongly heated in air, magnesium sulphate decomposes, leaving the oxide. Double salts with alkali metals are readily formed, e.g. $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ is *schönite*, a Stassfurt mineral, which is deposited from a hot solution on cooling (although K_2SO_4 is less soluble). A solution of the anhydrous sulphate in concentrated sulphuric acid deposits crystals of $\text{Mg}(\text{HSO}_4)_2$.

Double salts in solution are almost completely decomposed into the single salts, as is shown by the depression of freezing point. They are so distinguished from **complex salts** such as $\text{K}_4\text{Fe}(\text{CN})_6$, which retain their constitution in solution and ionise accordingly:



Isomorphous mixtures or **mixed crystals**, e.g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, differ from double salts by having a variable composition, and they may be represented by such formulae as $(\text{Fe}, \text{Mg})\text{SO}_4 \cdot 7\text{H}_2\text{O}$.

Magnesium is separated from the alkalis by adding baryta-water, when $\text{Mg}(\text{OH})_2$ is precipitated. The excess of baryta is precipitated from the filtrate by saturation with carbon dioxide, when BaCO_3 is formed, leaving the alkali carbonates in solution. The precipitate of $\text{Mg}(\text{OH})_2$ is washed, dissolved in dilute hydrochloric acid, and precipitated as MgNH_4PO_4 .

ZINC

History.—Plato (400 B.C.) refers to *orichalcum*, probably *brass*, an alloy of zinc and copper no doubt obtained by heating copper with an ore known as *cadmia* and charcoal.

Brass of the period 1500 B.C. containing 23 per cent of zinc and 10 per cent of tin, was found at Gezer in Palestine. Deposits of *calamine*, native zinc carbonate, occur in the old silver mines of Laurion in Greece. Strabo (about 7 B.C.) describes the preparation of the metal, which he calls mock-silver, by heating the oxide with coal. A statuette from Thrace of about his time consists of zinc with lead and a little iron.

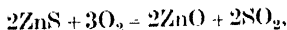
The name *spelter* is used for the metal by Boyle, and Libavius about 1600 describes zinc, which he says was a peculiar kind of tin called *calaim* brought from the East Indies. The extraction of zinc seems to have been carried out at an early period in China. The real nature of brass was not clear until Kunckel observed that: "calamine allows its mercurial [*i.e.*, metallic] part to pass into the copper and form brass." Zinc was identified as the metal from blende (ZnS) by Homberg in 1695; the extraction of the metal from calamine was effected by Isaac Lawson in 1730, and in 1743 the first European zinc works was started by John Champion at Bristol.

Occurrence.—Zinc occurs as *blende* (*sphalerite* in the U.S.A.) ZnS, usually coloured yellow or brown by iron ("black-jack" of the miners) and possessing a characteristic resinous lustre. It is found in England, in many parts of Europe and America, in Rhodesia, Burma and New South Wales. The carbonate occurs as *calamine* (*smithsonite* in the U.S.A.) ZnCO₃. *Electric calamine* or *hemimorphite* (*calamine* in the U.S.A.) is a silicate Zn₂SiO₄.H₂O. The anhydrous silicate is *willemite*, which is used in making fluorescent screens for X-rays and α-rays.

Zinc oxide *zincite* or *red zinc ore* ZnO is rare, but zinc ferrite Zn(FeO₂)₂ or ZnO.Fe₂O₃ forms the important *franklinite* deposit of Franklin Furnace, New Jersey, mostly worked for zinc oxide and the manganese it contains. The New South Wales ore contains galena and is first "concentrated" by flotation (p. 6). Certain varieties of pyrites, *e.g.* Westphalian, contain zinc sulphide. Traces of zinc occur as an organic compound in animal cells and in snake venom (0.11–0.56 per cent).

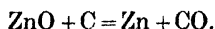
Metallurgy.—Zinc is a volatile metal and can be distilled. In 1807 zinc smelting was begun at Liège in Belgium and later on spread to Silesia. These two processes are still in use and are called the *Belgian process* and the *Silesian process*, respectively. In Europe blende is mostly smelted.

The blende is first roasted and the sulphur dioxide produced may be used to make sulphuric acid. External heating has to be used, the blende being raked in a series of muffles through which air circulates, or on a furnace hearth. Care must be taken that only zinc oxide is produced:



since the sulphate is very stable and if formed would give sulphide in the subsequent reduction, leading to considerable loss. Some sulphate is always formed but is decomposed at the high temperature used. The roasted ore is next mixed with half its weight of powdered coal and

charged into small fire-clay retorts which are strongly heated. Zinc distils :



The Belgian retorts consist of fire-clay tubes closed at one end and set in a furnace, sloping towards the open end. An iron tube (called a "prolong") is luted into the open end with clay and serves to condense the zinc. The Silesian retorts (Fig. 370) are fire-clay muffles, to which a fire-clay condenser



FIG. 370.--Zinc furnace.

tube and an iron air-cooled "prolong" are luted. The newer Belgo-Silesian furnaces employ three rows of muffles, one above the other, the lower row supported along their length on the hearth and the two upper rows only at the ends. They are fired with gas. In all cases 10-25 per cent of the zinc is lost, about half in the ash and half as vapour, and a considerable proportion of the metal is obtained in the form of a powder mixed with oxide known as *zinc dust*. Continuous vertical furnaces are also used and sometimes the poor-grade oxidised ores are roasted to form zinc oxide fume which is collected and then reduced in retorts.

Commercial zinc is called *spelter* and contains about 97-98 per cent of zinc, 1-3 per cent of lead, up to 0.1 per cent of iron, more rarely cadmium and some arsenic. Pure zinc is prepared by electrolysis of an acid solution of pure zinc sulphate with a high current density. It is essential that the electrolyte shall be free from cobalt. Indium is recovered as a by-product from some ores. The electrolyte may be prepared from roasted blende, dissolved in dilute sulphuric acid, followed by purification of the solution, iron, aluminium, arsenic, antimony, and silica being precipitated by milk of lime, and copper and cadmium by zinc dust.

Very pure zinc (99.99 per cent) is made by rectification distillation. The main impurities are iron (b. pt. 2800°), lead (b. pt. 1620°) and cadmium (b. pt. 767°). The cadmium can be completely vaporised below the boiling point of zinc (905°). Molten zinc is fed into a column heated above its boiling point, when most of the zinc and all the cadmium distil and are condensed, the iron and lead collecting in the metal flowing from the base of the column. The molten zinc-cadmium alloy is similarly treated in a second column, when cadmium distils and pure zinc flows from the base of the column.

For use in the laboratory zinc is granulated by melting in a clay crucible and pouring into a bucket of water. Zinc foil or sheet is prepared by heating the metal to 100°-150°, when it becomes soft, and rolling it.

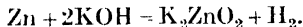
Zinc dust is made by atomising molten zinc with a blast of air, and consists of small spheres of zinc coated with oxide. It always contains oxide.

but the good kinds may contain over 90 per cent of metallic zinc. Zinc nitride may be present. Zinc oxide may be removed by washing with very dilute hydrochloric acid, water and alcohol, and drying.

Properties.—Zinc is crystalline (hexagonal), moderately hard and brittle, and has a bluish-white colour. Its vapour density corresponds with the formula Zn. It readily burns in air when the turnings are heated in a flame, or the metal is heated strongly in a crucible, producing a white cloud of oxide which settles out in the form of woolly flocks. These were called "Philosophers' wool", *nix alba*, or *pompholyx*, by the alchemists. A tassel of thin sheet zinc tipped with a little burning sulphur burns brilliantly in oxygen. The metal oxidises in moist air forming a greyish-white crust of the basic carbonate, and is attacked and dissolved by soft water, especially that containing peat acids, or sea water. The zinco-solvency of water is reduced by standing over limestone.

Zinc is more resistant to moist air than iron, and is used as a protection for this metal. The iron sheets or wire are cleaned by a sand-blast and "pickling" in dilute hydrochloric acid, and are dipped into molten zinc when an adherent coating of the latter is formed. This process is known as *galvanising* and the product as *galvanised iron*. Iron articles may also be coated with zinc by spraying or by heating them in zinc dust (*sherardising*). The zinc dissolves before iron in presence of oxygen and moisture, since it is more electropositive than iron. The metal is also used for the negative electrodes of voltaic cells.

Zinc dissolves in dilute acids evolving hydrogen (except with nitric acid) and producing zinc salts containing the cation Zn^{++} . It also dissolves readily in hot solutions of potassium or sodium hydroxides (magnesium is insoluble), evolving hydrogen and forming solutions of *zincates* (the solid zincates $Na_2ZnO_2 \cdot 4H_2O$ and $NaHZnO_2 \cdot 3H_2O$ are described) :



Ordinary zinc dissolves readily in dilute acid, whereas some varieties of very pure metal dissolve slowly unless a few drops of copper sulphate or platinum chloride solution are added. Metallic copper or platinum is precipitated on the zinc and forms a galvanic couple, from the insoluble part of which hydrogen is readily evolved. Sturgeon (1830) found that the amalgamated metal is hardly attacked by acids; the commercial varieties are more resistant when amalgamated than the amalgamated pure metal (J. N. Friend, 1929).

Brass.—Copper and zinc form two definite compounds Cu_2Zn_3 and (probably) $CuZn$, and also two types of solid solutions called α - and β -brass. The brasses are of two main types: (1) those with more than 64 per cent of copper, which are homogeneous α -solutions; (2) those with 55–64 per cent of copper, composed of α - and β -solutions. Brasses of 70 copper + 30 zinc typify (1) and those of 60 copper + 40 zinc typify (2).

The effect of adding zinc to copper is to increase progressively the strength, toughness and hardness of the alloy up to 36 per cent of zinc, after which the increase in strength is more marked. Zinc mixes when fused with tin, copper and antimony in all proportions, but is only partially miscible with lead and bismuth. Various alloys containing from 2 to 36 per cent of zinc are made.

Gilding metal (3-8Zn), *tombac* (gold colour : 10-18Zn), *pinchbeck* (dark gold colour, 7-11Zn) are low in zinc. *Cartridge brass* is 70Cu + 30Zn, *common brass* for sheets is 2Cu to 1Zn. All α -brasses are ductile and can be worked cold : tin, lead and aluminium are often added for special purposes, e.g. for condenser tubes the alloy contains 29Zn and 1Sn. The usual *casting brass* contains 27Zn, 2Pb and 1Sn. *Muntz metal* contains 60-62 Cu and 40-38 Zn. Brass with 1.5 to 2 per cent of lead machines better ; for free turning qualities 2 to 3 per cent may be present. Manganese is added to 60 : 40 brass to increase the strength but often only traces are present in *manganese bronze*. A brass containing 2 per cent of manganese takes a dark brown or chocolate colour when extruded hot, due to a film of oxide, and is used for window-frames. *Nich metal* is 60Cu, 2Fe, and 38Zn ; *Sterro metal* contains more iron. High tensile brasses contain nickel in place of copper, e.g. 50Cu, 45Zn and 5Ni. If the zinc is kept at 45, the tensile strength increases up to 12 per cent Ni. Alloys with 45 each of copper and zinc and 10 of nickel are white (*nickel brasses*) and can be worked hot.

ZINC COMPOUNDS

Anhydrous zinc chloride $ZnCl_2$, a soft white solid (m. pt. 365° , b. pt. 730) subliming at a red heat in white needles is formed by passing chlorine or hydrogen chloride over heated zinc or by distilling the metal with mercuric chloride : $HgCl_2 + Zn \rightarrow Hg + ZnCl_2$.

Chlorine decomposes zinc oxide at a dull red-heat forming the chloride with evolution of oxygen. Zinc chloride solution is formed by dissolving zinc or its oxide or basic carbonate in hydrochloric acid. On evaporation a syrupy liquid is obtained : if a little concentrated hydrochloric acid is added, small deliquescent crystals of $ZnCl_2 \cdot H_2O$ separate. If the aqueous solution is evaporated to dryness, zinc oxychlorides $Zn(OH)Cl$ and Zn_2OCl_2 are formed to some extent, but if the dry mass is distilled at a red heat the anhydrous chloride passes over. By evaporation in a current of hydrochloric acid gas the fused salt is obtained and may be cast into sticks. Zinc chloride is very deliquescent and is soluble in water, alcohol, ether, acetone and pyridine.

An oxychloride $Zn(OH)Cl$ or Zn_2OCl_2 is produced by mixing a syrupy solution of the chloride with zinc oxide and sets rapidly to a very hard mass used as a dental stopping. Concentrated zinc chloride solution is used for impregnating timber to prevent its destruction by micro-organisms ("dry rot"), and as a caustic (it dissolves proteins). In timber-preserving zinc chloride is being replaced by sodium fluoride.

A solution of zinc chloride is used as a flux in soldering. On heating it liberates hydrochloric acid, which dissolves metallic oxides and keeps the metal surface clean. Zinc chloride is used, like magnesium chloride, for "filling" (i.e. weighting) cotton goods. The compound $\text{ZnCl}_2 \cdot 2\text{NH}_3$ is formed as crystals in Leclanché batteries, and zinc chloride absorbs ammonia gas to form $\text{ZnCl}_2 \cdot 4\text{NH}_3$. These are hydrolysed by water, with deposition of white oxychlorides which dissolve in dilute hydrochloric acid.

Zinc bromide ZnBr_2 (m. pt. 390°) and zinc iodide ZnI_2 (m. pt. 450°) are formed from the elements in presence of water. Zinc fluoride $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ is sparingly soluble.

Zinc oxide ZnO is formed by burning zinc vapour in air: it is called *zinc white* and is used as a pigment. It is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and heating the basic carbonate. It is a white powder which becomes sulphur-yellow on heating, the colour disappearing on cooling. A crystalline oxide is formed by the action of steam on zinc at a red heat. Zinc oxide sublimes appreciably at 1400° . It is reduced by *dry* hydrogen above 450° . Zinc oxide dissolves readily in acids producing zinc salts, and in alkalis forming *zincates*. It is therefore an *amphoteric oxide* (p. 811).

Zinc oxide is used as a pigment, as an absorbent in surgical dressing, as a "filling" for rubber, and in the preparation of *Rumman's green*, which is obtained by heating zinc oxide with a solution of cobalt nitrate and is cobalt zincate CoZnO_2 in solid solution in zinc oxide. The formation of this green substance is the basis of the blowpipe test for zinc.

Zinc hydroxide Zn(OH)_2 is formed as a white flocculent precipitate on adding alkali hydroxide or ammonia to a solution of a zinc salt. Ammonia does not precipitate zinc in presence of ammonium chloride. Crystals are obtained by allowing a zinc plate and iron turnings to stand in concentrated ammonia. It can be dried at 85° but loses water at higher temperatures. Zinc hydroxide is practically insoluble in water, but the precipitate is readily soluble in excess of alkali, forming a solution of a zincate. Ammonia also dissolves it, forming a complex hydroxide:
$$\text{Zn(NH}_3)_4(\text{OH})_2 \cdot \text{Zn(NH}_3)_4^{++} + 2\text{OH}^-.$$

By the action of cooled 30 per cent hydrogen peroxide on zinc oxide, a white or yellow powder is obtained, which is believed to be a hydrated zinc peroxide $\text{ZnO}_2 \cdot \text{Aq}$. It is used in surgery and dermatology.

Zinc and zinc oxide dissolve in water containing carbon dioxide. Sodium carbonate or bicarbonate precipitates white zinc carbonate from a solution of a zinc salt; on standing under the mother liquor the amorphous precipitate forms $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$. On washing, this forms the basic carbonate $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$. The precipitate of zinc

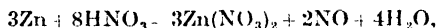
carbonate is soluble in concentrated potassium carbonate solution but is precipitated on dilution. A crystalline carbonate is formed by heating zinc sulphate solution with sodium bicarbonate in a sealed tube at 160°. When boiled with sodium carbonate solution, zinc carbonate or basic carbonates form zinc oxide. Zinc carbonate begins to decompose at 140° and decomposition is rapid at 300° : $\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2$.

Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is obtained by dissolving the metal, oxide or carbonate in dilute nitric acid and crystallising. It is deliquescent and is soluble in alcohol. The anhydrous nitrate is formed by heating the hydrate at 130°–135° in a current of carbon dioxide and N_2O_5 vapour : it decomposes at 140°.

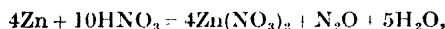
The action of nitric acid on zinc is complex ; with concentrated acid nitrogen peroxide is evolved :



with diluted acid, nitric oxide :



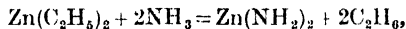
whilst with very dilute acid nitrous oxide may be evolved :



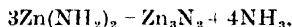
and the acid is also reduced to ammonia :



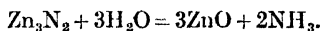
Ammonia and a solution of zinc ethyl in dry ether give **zinc amide** $\text{Zn}(\text{NH}_2)_2$:



and on heating to dull redness this forms **zinc nitride** Zn_3N_2 :

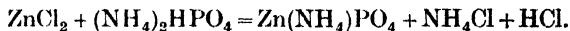


a grey or green powder vigorously decomposed by water (Frankland, 1858) :



Zinc phosphide Zn_3P_2 is a grey solid formed by heating zinc and phosphorus : it evolves phosphine with acids.

Zinc phosphate $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ is obtained by heating a solution of zinc sulphate and Na_2HPO_4 , in the form of pearly scales insoluble in water and dilute acids. On heating it forms the infusible anhydrous salt. **Zinc ammonium phosphate** $\text{Zn}(\text{NH}_4)\text{PO}_4$ is precipitated from neutral solutions of zinc salts by ammonium phosphate (*cf.* Mg) :

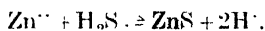


When dried at 105° it is ZnNH_4PO_4 and may be weighed in the gravimetric determination of zinc. On heating gradually in an open crucible it forms white **zinc pyrophosphate**, $\text{Zn}_2\text{P}_2\text{O}_7$:

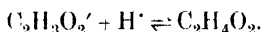


Zinc sulphide ZnS occurs in cubic crystals as *blende* and more rarely in hexagonal crystals as *wurtzite*. Wurtzite may be formed from zinc vapour and hydrogen sulphide. An artificial phosphorescent sulphide (*Sidot's blende*) formed on heating the precipitated sulphide to whiteness in a covered crucible is used in making fluorescent screens for X-ray and radioactivity work. Perfectly pure zinc sulphide is not fluorescent. Massive zinc and sulphur do not react easily on heating, but the mixed powders react with incandescence when heated and the mixture may detonate on percussion. Zinc sulphide is easily obtained by heating zinc oxide with sulphur, or as a white precipitate on adding ammonium sulphide to a solution of a zinc salt; it is insoluble in excess of reagent but dissolves in all dilute mineral acids, but not in acetic acid (*cf.* MnS).

If hydrogen sulphide is passed into a solution of zinc sulphate, zinc sulphide is at first precipitated but owing to the acid formed the precipitation soon ceases:



If sodium acetate is added to the solution, the concentration of hydrogen ions is kept low by the formation of the very weak acetic acid:

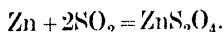


If nickel and cobalt are present, they are precipitated only after all the zinc is precipitated.

The best conditions for precipitation of zinc sulphide are at 50°-100° in a solution buffered to pH 2 to 3 by ammonium sulphate and formate and formic acid.

Two modifications of zinc sulphide are precipitated, one (α -ZnS) in acid solution and another (β -ZnS) in alkaline solution, the second form having five times the solubility of the first. In acid solutions the precipitation of zinc sulphide shows a period of induction, which is longer the more acid is the solution. In some cases no precipitate is formed, although zinc sulphide is almost insoluble in the strength of acid used. Other sulphides, *e.g.* CuS and CdS, bring about simultaneous precipitation of the zinc sulphide.

Zinc dissolves in sulphurous acid solution to form zinc hyposulphite ("hydrosulphite") ZnS_2O_4 which is a powerful reducing agent:



Zinc sulphate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, isomorphous with Epsom salt, is called *white vitriol*. It is very soluble in water. It is the commonest salt of zinc and is prepared by dissolving the metal, oxide or carbonate in dilute sulphuric acid, evaporating, and crystallising below 39°. Above 39° $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is deposited. On heating $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ at 100° $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ is left, and at 280°, or lower in a current of dry air, anhydrous ZnSO_4 is formed. When heated above 767° sulphur trioxide is evolved and zinc oxide remains: $\text{ZnSO}_4 = \text{ZnO} + \text{SO}_3$. Double salts of zinc sulphate,

e.g. $K_2SO_4, ZnSO_4, 6H_2O$, are easily prepared. A dilute solution of white vitriol is used as an eye lotion, and zinc sulphate is used in the manufacture of lithopone (p. 767).

Ammine compounds similar to those of copper are formed with zinc salts e.g. $Zn(NH_3)_4Cl_2, H_2O$, $Zn(NH_3)_4SO_4, H_2O$, $Zn(NH_3)_5SO_4$, etc.

The atomic weight of zinc was determined by precipitating pure zinc bromide with silver nitrate.

Phosphorescence.—Reference has been made to the phosphorescence of calcium sulphide and nitrate, and of barium and zinc sulphides, i.e. the property which these materials possess of shining after exposure to light, especially sunlight. This is used in the preparation of *luminous paint*. Pure compounds do not phosphoresce; the property is due to traces of heavy metals such as bismuth, lead, copper, molybdenum, tungsten, uranium, etc. Phosphorescent calcium sulphide is obtained by heating a mixture of 100 parts of calcium carbonate with 30 parts of powdered sulphur for an hour to dull redness in a closed crucible. The mass is cooled, and triturated with alcohol to which sufficient bismuth nitrate is added to give 1 part of bismuth to 10,000 of calcium sulphide. The mass is dried in the air and heated to dull redness for two hours. It is then slowly cooled.

Other phosphorescent masses are prepared by heating the mixtures *A* below, powdering the product, moistening with the solutions *B*, and re-heating (all weights in grams):

1. *Violet light*: *A*: CaO (powder) 20, S 6, starch 2, Na_2SO_4 0.5, K_2SO_4 0.5. *B*: 2 ml. of 0.5 per cent $Bi(NO_3)_3$ solution; 0.5 ml. of aqueous Tl_2SO_4 .

2. *Deep blue light*: *A*: CaO 20, $Ba(OH)_2$ 20, S 6, K_2SO_4 1, Na_2SO_4 1, Li_2CO_3 2, starch 2. *B*: 2 ml. of 0.5 per cent alcoholic $Bi(NO_3)_3$ solution + 2 ml. of 1 per cent $RbNO_3$ solution.

3. *Bright green light*: *A*: $SrCO_3$ 40, S 6, Li_2CO_3 1, As_2S_3 1. *B*: 2 ml. of 0.5 per cent $TlNO_3$ solution.

4. *Deep orange-red light*: *A* (only): $BaCO_3$ 40, S 6, Li_2CO_3 1, Rb_2CO_3 0.47

5. *Golden yellow light* (unusual): $BaCO_3$ 25, $Sr(OH)_2$ 15, S 10, starch 3, Li_2SO_4 1, MgO 1, $Th(SO_4)_2$ 2 ml. of 0.5 per cent solution, $CuSO_4$ 3 ml. of 0.4 per cent solution. Heat 40 minutes.

CADMIUM

History.—A specimen of zinc oxide which had a yellow colour, although free from iron, was found by Stromeyer in 1817 to contain the oxide of a new metal to which he gave the name cadmium, from *cadmia*, the old name for zinc ore (*καδμεία*, in Dioskourides).

Occurrence.—Most zinc ores contain small amounts of cadmium. Blende may contain 2-3 per cent of cadmium and calamine up to 5 per cent, but the average is less than 0.5 per cent. The only mineral, the sulphide *greenockite* CdS , is rare.

Cadmium and its compounds.—Cadmium is more volatile than zinc as the boiling points of the metals in the zinc group decrease with rising atomic weight. Hence the first portions of dust collecting in the re

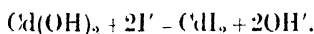
receivers of zinc furnaces in which ores containing cadmium are reduced contain most of the cadmium in the form of brown oxide CdO , mixed with zinc oxide. The dust is heated strongly with coal in retorts having long sheet-iron tubes as adapters. The distillate may contain 20 per cent or more of cadmium oxide and is distilled with charcoal in small iron or clay retorts to give the metal. In America much cadmium is extracted from the fumes from lead and copper furnaces, and some from the solutions used in making electrolytic zinc, from which it is precipitated by zinc.

Cadmium is a soft bluish-white metal of low melting point; it "cries" like tin when bent. The vapour density corresponds with the formula Cd . It is slowly oxidised in air, forming a protective coating, and very thin deposits of plating are used to protect iron and steel from rust. They may be heat-treated to form an alloy with the iron. Cadmium is a constituent of some fusible alloys (p. 873). A small amount of cadmium is alloyed with copper for electricity transmission wires; it is added in small amounts to aluminium for casting and is also added to silver to decrease staining. It is used in antifriction alloys and in solders in place of tin. Cadmium amalgam, formerly used for dental stoppings, forms the cathode in the Weston standard cell.

Cadmium dissolves slowly in dilute hydrochloric and sulphuric acids and easily in dilute nitric acid, forming colourless salts, which are poisonous. Cadmium chloride $2\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ is efflorescent and is not hydrolysed by water. The halogen salts are all soluble in water but are only feebly ionised, forming complex ions in the metal exists in the negative ion:



Insoluble cadmium salts, *e.g.* CdS , therefore readily dissolve in a solution of potassium iodide, since practically all the cadmium ions are removed as complex ions or un-ionised salt and the solubility product of the cadmium salt is not exceeded:



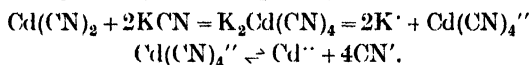
If a concentrated solution of potassium iodide is added to an ammoniacal solution of a cadmium salt, a white precipitate of $\text{Cd}(\text{NH}_3)_2\text{I}_2$ is formed. Copper salts give no precipitate. Cadmium iodide is used in photography.

The brown cadmium oxide CdO is formed by burning cadmium in air, or by heating the hydroxide, carbonate or nitrate. White cadmium hydroxide $\text{Cd}(\text{OH})_2$ is precipitated by alkali hydroxide from a solution of cadmium nitrate or sulphate; it is insoluble in excess but dissolves in ammonia forming a complex hydroxide $\text{Cd}(\text{NH}_3)_4(\text{OH})_2$.

Cadmium hydroxide attracts carbon dioxide from the air and cadmium carbonate CdCO_3 is precipitated by adding excess of ammonium carbonate to a solution of cadmium chloride, then just enough ammonia to dissolve the precipitate and heating on the water bath. The white precipitate formed by alkali carbonates from solutions of cadmium salts contains some hydroxide.

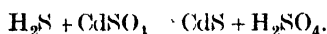
Cadmium cyanide $\text{Cd}(\text{CN})_2$ readily forms a soluble complex salt with potassium cyanide, but the complex ion is so much ionised that a

precipitate of cadmium sulphide is formed in the ammoniacal solution by hydrogen sulphide (*cf.* copper, p. 727) :



Cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is deliquescent and is soluble in alcohol.

Cadmium sulphide CdS is obtained as a bright-yellow precipitate (used by artists under the name of *cadmium*) by passing hydrogen sulphide into a solution of a cadmium salt which is not too strongly acid. It crystallises in forms which may be either yellow or red. In more acid solutions a *red* form is precipitated—perhaps only because the particles are larger. If the acid concentration exceeds 1.3 normal the sulphide is not precipitated :



According to Treadwell, a double salt, *e.g.* $\text{Cd}_2(\text{Cl}_2\text{S})_2$, is always present in the precipitate. Cadmium sulphide is insoluble in ammonium sulphide but is soluble in boiling dilute sulphuric acid.

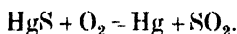
Cadmium sulphate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ is formed in large crystals by the spontaneous evaporation of a solution of cadmium or cadmium oxide in dilute sulphuric acid. It is used in the solution in the Weston cell.

The so-called “cadmous” compounds, Cd_2O , CdCl , are probably mixtures of bivalent cadmium compounds and finely-divided metallic cadmium.

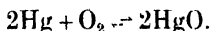
MERCURY

History.—Metallic mercury is mentioned by Aristotle and Theophrastus as “liquid silver” and Dioscourides calls it “silver water” or *hydrargyros*, which Pliny calls *hydrargyrum* (the origin of the symbol Hg). The name “quicksilver” (*argentum vivum*) is also used by Pliny. In the Roman period the metal was made, as at present, by roasting the native sulphide from Spain, which was also used as a red pigment.

Metallurgy.—Small quantities of mercury occur native or as amalgams and halogen compounds, but the only important ore is *cinnabar*, mercuric sulphide HgS , a red or black mineral found in Almaden (Spain), Idria, Monte Amiata (Italy), and in smaller amounts in Peru, California, Mexico, China, and Japan. In the extraction of the metal the cinnabar is roasted in a current of air :



Mercury undergoes only slow oxidation in air at 300° ; it was used in Lavoisier's famous experiment (p. 33) to extract the oxygen from air, the resulting mercuric oxide being decomposed at a higher temperature into mercury and oxygen :



In the preparation by roasting cinnabar in air, the mercury vapour carried on with the gas is condensed by cooling.

In modern works the lump ore is mixed with fuel and fed to the top of a shaft furnace (Fig. 371) and the mercury vapour is condensed in cooled Y-shaped tubes. Powdered ore is roasted in a vertical shaft with inclined shelves sloping alternately in opposite directions, flames and heated air passing upwards over the ore, and the mercury vapour is condensed in brick chambers and flues.

In the older process of extraction, now used only at Almaden, the ore is roasted in a shaft by a fire, and the vapours pass through openings into a series of stoneware *udells* arranged first in a descending and then in an ascending position on brick arches. The condensed mercury flows from these into a channel and then into cisterns. The metal is exported in iron bottles holding about 75 lb.

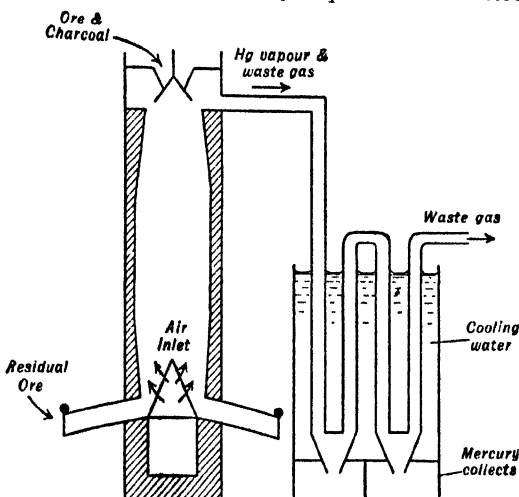
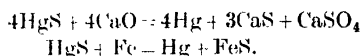


FIG. 371.—Mercury shaft furnace.

The old processes in which cinnabar was distilled with lime or iron filings are in use only for very rich ore :



The uses of mercury have diminished. It has been replaced by silvering in making mirrors, and the amalgamation method for the extraction of gold and silver is being displaced by the cyanide processes. Its other uses (p. 788) require only small amounts. A curiosity is the use of an artificial radioactive isotope made from gold in some fluorescent lamps.

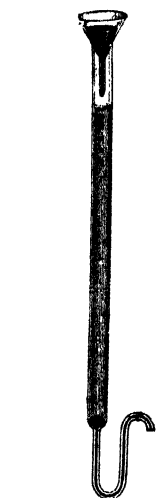


FIG. 372.—Purification of mercury.

Commercial mercury contains lead and sometimes zinc, tin and bismuth; it leaves a "tail" when it runs over glass and forms a black scum when shaken with air. It is purified by running it several times in a fine stream through a column of 5 per cent nitric acid containing some mercurous nitrate (Fig. 372), when the lead, etc. (which are more easily oxidised than mercury) dissolve in the acid.

It may also be shaken with a concentrated solution of potassium permanganate in 6*N* sulphuric acid containing a little ferric chloride. The mercury is then distilled in a vacuum with a still surface, as if it "umps" impurities are carried over (Fig. 373).

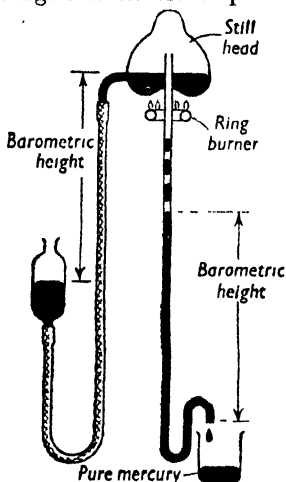


FIG. 373.—Mercury still.

Properties.—Mercury is a silver-white liquid metal of high density (13.5955 at 0°) which freezes to a malleable solid in solid carbon dioxide and ether. It boils at 357° and the vapour is monatomic (see p. 110). The metal has only a small vapour pressure at room temperature (<0.0002 mm. at 0°, 0.008 mm. at 40°, 0.270 mm. at 100°) and in laboratory air it is covered with a film so that it is practically non-volatile. The vapour may be seen rising from warm mercury by its fluorescence in

ultra-violet light, and as it is very poisonous mercury should never be heated in an open vessel in the laboratory.

Mercury is used in making thermometers and barometers, mercury vapour lamps, and amalgams: its compounds (especially mercuric oxide and mercurous and mercuric chlorides) are used in medicine, and the fulminate is used in detonators.

Mercury is transparent in very thin films, and transmits blue light.

When triturated with fats and powders such as chalk or sugar, mercury is divided into very minute globules (0.002 mm.) and such grey preparations are used in medicine. A brown colloidal solution is formed by reducing mercurous nitrate by stannous nitrate in presence of ammonium citrate.

Mercury forms amalgams with most metals and these often contain definite compounds; iron is amalgamated with difficulty, by grinding iron powder with water and mercuric chloride. Copper amalgam becomes plastic when warmed at 100° and rubbed in a mortar; it hardens again after a few hours and is used in stopping teeth. Mercury in silver nitrate solution forms a tree-like growth (*arbor Dianae*) of silver amalgam. Mercury easily whitens gold and copper.

Mercury combines with oxygen and sulphur when heated, with chlorine at the ordinary temperature, and with iodine on grinding in a mortar; with excess of mercury green mercurous iodide is formed, with excess of iodine red mercuric iodide. The metal is not attacked by hydrochloric acid in absence of air nor by cold concentrated or hot dilute sulphuric acid. Hot concentrated sulphuric acid converts it into

mercuric sulphate. Mercury dissolves in dilute and concentrated nitric acid, forming mercurous and mercuric nitrates, respectively.

Mercury forms two series of compounds, the mercurous and the mercuric compounds. In the mercurous compounds HgX it is apparently univalent but they probably have the doubled formulae Hg_2X_2 and contain the bivalent group $--Hg--Hg--$ in which mercury is bivalent. The mercuric compounds HgX_2 contain bivalent mercury $--Hg--$.

The constitution of the mercurous compounds has been the object of several experiments. H. B. Baker found that the vapour density of carefully dried mercurous chloride corresponds with the doubled formula Hg_2Cl_2 , which was also found by Beckmann from the freezing point of a solution of mercurous chloride in fused mercuric chloride. Ogg, from physico-chemical considerations, concluded that the mercurous ion has the formula Hg_2^{++} .

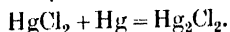
The vapour density of undried mercurous chloride corresponds with the formula $HgCl$, but Harris and Victor Meyer (1894) showed that the vapour is dissociated: $Hg_2Cl_2 \rightleftharpoons Hg + HgCl$. If the vapour is contained in a porous earthenware tube, mercury diffuses out and condenses in globules, whilst the residue in the tube contains an excess of $HgCl_2$. If gold leaf is introduced into the vapour, it is amalgamated by the free mercury. Salts of mercury do not react with gold.

MERCUROUS COMPOUNDS

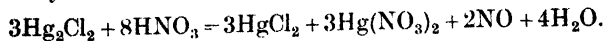
Mercurous fluoride Hg_2F_2 is a yellow crystalline solid, soluble in water, formed by dissolving mercurous carbonate in hydrofluoric acid.

Mercurous chloride Hg_2Cl_2 occurs native as *horn quicksilver*. It is formed by the action of chlorine on excess of mercury and as a white precipitate on addition of hydrochloric acid or sodium chloride to mercurous nitrate solution. To obtain a pure product, excess of chloride is used and the solution heated.

Mercurous chloride is called *calomel* and is used in medicine as a purgative. It is prepared by subliming in an iron pot a mixture of mercuric chloride and metallic mercury, made by triturating the substances in a mortar. The crust of calomel formed on the lid of the pot is ground to powder and boiled with water to remove the very poisonous mercuric chloride, some of which always sublimes unchanged:



Mercurous chloride is very sparingly soluble in water (0.4 mg. per lit. at 20°); it dissolves to some extent in solutions of chlorides and in concentrated hydrochloric acid but is decomposed into mercuric chloride and mercury. It dissolves in hot concentrated nitric acid:



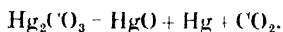
Aqueous ammonia converts it into a black powder, formerly regarded as

a definite compound Hg_2ClNH_2 , but probably consisting of a mixture of black finely-divided mercury and the mercuric compound called "insoluble white precipitate" (p. 795), viz. $\text{Hg} + \text{HgCl.NH}_2$. A similar black precipitate of $\text{Hg} + \text{HgNO}_3.\text{NH}_3$ is formed when ammonia is added to mercurous nitrate solution.

Mercurous bromide Hg_2Br_2 is a white insoluble powder similar to calomel. **Mercurous iodide** Hg_2I_2 is formed as a green powder by triturating excess of mercury and iodine. On heating it becomes yellow. The pure iodide, formed by boiling excess of iodine with mercurous nitrate solution containing a little nitric acid and cooling, consists of transparent yellow crystals which blacken on exposure to light: $\text{Hg}_2\text{I}_2 = \text{HgI}_2 + \text{Hg}$.

Mercurous oxide Hg_2O is formed as a black powder by triturating calomel with sodium hydroxide solution or by precipitating a solution of mercurous nitrate with sodium hydroxide. It readily decomposes on warming or on exposure to light into mercury and mercuric oxide, and has been regarded as a mixture of mercuric oxide and finely-divided mercury, as its X-ray diagram indicates.

Mercurous carbonate Hg_2CO_3 is formed as a yellow precipitate on adding excess of potassium bicarbonate solution to mercurous nitrate solution and allowing to stand for a few days to decompose any basic nitrate. It decomposes on exposure to light or when gently heated:



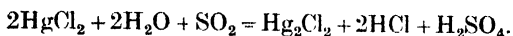
Mercurous nitrate $\text{Hg}_2(\text{NO}_3)_2.2\text{H}_2\text{O}$ is formed by the action of dilute nitric acid on excess of mercury in the cold, and readily crystallises from the solution on standing. If water is added to the crystals a white precipitate of basic nitrate is formed, which redissolves in dilute nitric acid. A little mercury is usually kept in the solution to prevent oxidation to the mercuric compound. A crystalline basic nitrate with the formula $3\text{Hg}_2(\text{NO}_3)_2.2\text{Hg}_2\text{O}.2\text{H}_2\text{O}$ is called *Marignac's salt*. Mercurous nitrate decomposes on heating into nitrogen dioxide and mercuric oxide: $\text{Hg}_2(\text{NO}_3)_2 = 2\text{HgO} + 2\text{NO}_2$.

Mercurous sulphide Hg_2S is formed by the action of carbon dioxide and hydrogen sulphide on dry mercurous chloride at -10° . It is decomposed by water, and the precipitate from solutions is $\text{Hg} + \text{HgS}$.

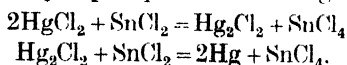
Mercurous sulphate Hg_2SO_4 is formed by warming an excess of mercury with concentrated (or fuming) sulphuric acid and deposits as a coarse crystalline powder on cooling. It is formed as a white precipitate by adding sulphuric acid to a solution of mercurous nitrate. It tends to hydrolyse when washed and a greenish-yellow basic salt with the formula $\text{Hg}_2\text{SO}_4.\text{Hg}_2\text{O}.\text{H}_2\text{O}$ is formed. According to Hulett (1904) the pure sulphate is best obtained by electrolysis with a mercury anode in dilute (1 : 6) sulphuric acid. Mercurous sulphate is used as a depolariser in the Weston cell.

MERCURIC COMPOUNDS

The mercuric compounds HgX_2 are formed by the oxidation of mercurous compounds. Calomel dissolves in aqua regia forming mercuric chloride HgCl_2 . The mercuric compounds may be reduced to mercurous compounds or to metallic mercury. Calomel is precipitated if sulphur dioxide is passed into a solution of mercuric chloride :



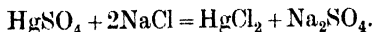
By the action of a solution of stannous chloride, white calomel or grey finely-divided mercury is precipitated according to the amount added :



All compounds of mercury are reduced to the metal on boiling with hydrochloric acid and copper foil ; the foil becomes white owing to amalgamation, and on heating it in a glass tube a sublimate of minute globules of mercury is formed. A similar sublimate is obtained if a mercury salt is heated with powdered charcoal and sodium carbonate.

Mercuric fluoride HgF_2 is formed by heating mercurous fluoride in dry chlorine at 275° or alone in a vacuum at 450° ; it is discoloured by traces of moisture. The hydrate $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$ is formed in white crystals by dissolving mercuric oxide in excess of hydrofluoric acid, and is easily hydrolysed by water to a yellow basic salt $\text{HgF}(\text{OH})$.

Mercuric chloride HgCl_2 , sometimes called *corrosive sublimate* on account of its volatility (m. pt. 277° , b. pt. 302°) and poisonous properties, is formed at the ordinary temperature by the action of chlorine on mercury, even when the materials are very dry. It is manufactured in this way, or by subliming a mixture of mercuric sulphate, common salt and a little manganese dioxide in a long-necked flat-bottomed flask heated in a sand-bath :



The manganese dioxide prevents the formation of calomel from some mercurous sulphate usually contained in the mercuric sulphate. The flask is broken after cooling and the cake of sublimate removed from the upper part.

Mercuric chloride forms colourless needles, sparingly soluble in cold but readily in hot water ; 100 parts of water dissolve at 0° 4.3, at 10° 6.57, and at 100° 54 parts of HgCl_2 . It is only very slightly ionised in solution (p. 237), and the solution (in which the salt has the normal mol. wt.) is slightly hydrolysed.

Mercuric chloride is a violent poison. The fatal dose is 0.2–0.4 gm. ; the antidote is the immediate administration of raw whites of eggs, followed by an emetic. The albumin is coagulated. Corrosive sublimate is used in preserving skins, as a bactericide, and in 0.1 per cent solution for sterilising the hands and instruments in surgery.

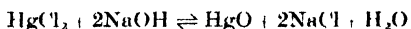
Mercuric chloride is readily soluble in alcohol and in ether (which extracts it from a solution of water). On account of its small ionisation, mercuric chloride is not decomposed by boiling concentrated sulphuric acid. It is not acted upon by nitric acid.

Mercuric chloride dissolves with evolution of heat in concentrated hydrochloric acid; the solution does not fume and on cooling deposits crystals of HHgCl_2 . With chlorides of alkali metals crystalline compounds are formed, e.g. KHgCl_3 and Na_2HgCl_4 , which are partly decomposed in solution and partly ionised into complex ions.



A solution of Na_2HgCl_4 is used instead of mercuric chloride as an antiseptic, since it is neutral in reaction and does not coagulate proteins. The ammonium salt $(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$ is called *sal alembroth*.

Alkalis precipitate a solution of mercuric chloride only incompletely, and mercuric oxide dissolves in hot solutions of alkali chlorides forming strongly alkaline liquids



This depends on the small ionisation of mercuric chloride, the concentration of mercuric ions from the dissociation of which is less than that in the very dilute saturated solution of mercuric oxide. The oxide therefore dissolves with formation of un-ionised mercuric chloride.

A mixture of mercuric chloride solution and oxalic acid (in presence of minute traces of iron salts) is reduced on exposure to light with measurable velocity depending on the intensity of the light: $2\text{HgCl}_2 + \text{C}_2\text{O}_4\text{H}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{CO}_2 + 2\text{HCl}$. Since the calomel may be filtered off and weighed, the reaction is used as a **chemical photometer** (Eder)

Phosphorus pentachloride combines with mercuric chloride to form the volatile crystalline compound $3\text{HgCl}_2 \cdot 2\text{PCl}_5$.

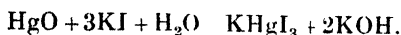
By boiling a solution of mercuric chloride with mercuric oxide, **mercuric oxychlorides** are formed, e.g. $2\text{HgCl}_2 \cdot \text{HgO}$ (red), $\text{HgCl}_2 \cdot 2\text{HgO}$ (black), $\text{HgCl}_2 \cdot 3\text{HgO}$ (*klemite*) (yellow), $\text{HgCl}_2 \cdot 4\text{HgO}$ (black).

Mercuric bromide HgBr_2 is similar to the chloride but less soluble, and is formed from mercury and bromine or by dissolving mercuric oxide in hydrobromic acid.

Mercuric iodide HgI_2 is formed as a yellow precipitate, which rapidly becomes scarlet, on adding the calculated amount of potassium iodide solution to mercuric chloride solution. On heating to 126° it is converted into another crystalline form which is yellow. The reverse change occurs on cooling, especially if the substance is rubbed. The yellow form is deposited on sublimation. Mercuric iodide is sparingly soluble in water (0.06 gm. per lit. at 25°) but more soluble in alcohol. It is not decomposed by dilute alkalis.

Mercuric iodide readily dissolves in solutions of mercuric chloride or potassium iodide. In the second case a complex compound, **potassium**

mercuri-iodide KHgI_3 is formed. The solution is not precipitated by alkalis since practically no mercuric ions are present, and mercuric oxide dissolves in a solution of potassium iodide to form a strongly alkaline liquid:

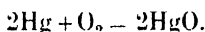


A solution of potassium mercuri-iodide containing excess of potassium hydroxide is used as a test for ammonia under the name of **Nessler's reagent**. With traces of ammonia a brown colour, with larger amounts a brown precipitate of $\text{NH}_2\text{Hg}_2\text{I}_3$, is formed.*

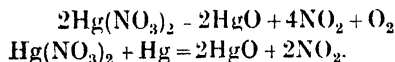
Nessler's reagent is prepared by dissolving 62.5 gm. of potassium iodide in 250 ml. of distilled water, and adding to the solution, except 5 ml. which is kept separate, a cold saturated solution of mercuric chloride until a faint permanent precipitate is formed. About 500 ml. will be required. The 5 ml. of KI solution are then added, and more HgCl_2 gradually until a slight permanent precipitate is formed. 150 gm. of potassium hydroxide are dissolved in 150 ml. of distilled water and the cooled solution added gradually to the other solution. The whole is made up to 1 litre. After settling, the clear solution, which should have a slight yellow colour, is decanted into a bottle covered with black varnish. It improves on keeping.

Mercury periodide HgI_6 is a brown substance said to be obtained by the action of mercuric chloride on an alcoholic solution of potassium tri-iodide. It readily loses iodine.

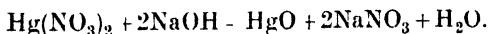
Mercuric oxide HgO is formed as a dense red crystalline powder (*mercurius praeipitatus per se*) by heating mercury for a long time just below its boiling point in a flask with a long neck open to the air:



The red crystalline oxide is also obtained (as "red precipitate") by heating mercuric nitrate or a mixture of mercuric nitrate and mercury (at higher temperatures the mercuric oxide decomposes):



Alkali hydroxide (*not* ammonia) gives a yellow precipitate of finely-divided mercuric oxide from a solution of mercuric nitrate; according to Ostwald this differs from the red oxide only by the particles being smaller:



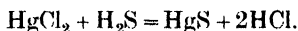
Mercury peroxide HgO_2 is obtained as an amorphous brick-red powder when hydrogen peroxide and then alcoholic potash are added to a solution of mercuric chloride in alcohol. It is fairly stable but is decomposed by water. The peroxide is also formed by the action of H_2O_2 on HgO at 0° , but decomposes with evolution of oxygen, leaving finely-divided mercury.

* This precipitate was previously given the formula $(\text{Hg}_2\text{O})\text{NH}_2\text{I}$ or $\text{NH}_2\text{Hg}_2\text{I} \cdot \text{H}_2\text{O}$

Mercuric carbonate is known only in the form of two basic salts, ochre-yellow $\text{HgCO}_3 \cdot 2\text{HgO}$, and brown $\text{HgCO}_3 \cdot 3\text{HgO}$, precipitated by adding mercuric nitrate solution to a large excess of KHCO_3 and K_2CO_3 solution, respectively.

Mercuric nitrate is obtained in large very deliquescent colourless crystals $2\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ by boiling mercury with excess of concentrated nitric acid, cooling and evaporating over quicklime in a desiccator. Mercuric nitrate is decomposed by water and the basic salt $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{HgO}$ is formed as a white powder. Mercuric nitrate is precipitated from solution by concentrated nitric acid.

Mercuric sulphide HgS occurs native as *cinnabar* and is the pigment *vermilion*. It is formed by subliming mercury with sulphur or by triturating mercury and sulphur with a little potassium or sodium hydroxide solution, when the black sulphide first produced slowly becomes red and crystalline. The red form is less soluble in alkali sulphides than the black and hence the latter when digested with sodium sulphide solution is slowly converted into scarlet vermilion. There is another crystalline form called *metacinnabar*. Mercuric sulphide is formed by precipitating a solution of the chloride with hydrogen sulphide :



The black precipitate of HgS first formed becomes white if shaken with the excess of mercuric chloride solution, the compound $\text{HgCl}_2 \cdot 2\text{HgS}$ being produced. The further action of H_2S changes this into a red and finally a black precipitate (HgS). The black precipitate becomes red on sublimation. It is insoluble in boiling concentrated hydrochloric acid or dilute nitric acid, but dissolves in aqua regia or in concentrated solutions of potassium or sodium sulphides, forming thio-salts, e.g. $\text{K}_2\text{HgS}_2 \cdot 5\text{H}_2\text{O}$ (white needles). It is easily soluble in a mixture of sodium hydroxide and ammonium sulphide. It is decomposed by boiling concentrated sulphuric acid :

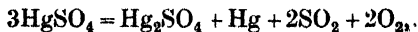


Mercuric sulphate HgSO_4 is obtained by boiling mercury with $1\frac{1}{2}$ times its weight of concentrated sulphuric acid and evaporating to dryness :



The white residue may be crystallised from sulphuric acid. With a small quantity of water it forms colourless crystals of $\text{HgSO}_4 \cdot \text{H}_2\text{O}$, but it readily hydrolyses, producing a yellow crystalline powder $\text{HgSO}_4 \cdot 2\text{HgO}$ sparingly soluble in water and called *turpeth mineral*.

Mercuric sulphate decomposes at 400° :



and when heated in a current of hydrogen chloride it is quantitatively converted into mercuric chloride.

Mercuric cyanide $\text{Hg}(\text{CN})_2$, which is only slightly ionised, is formed by dissolving mercuric oxide in aqueous hydrocyanic acid and crystallising; it is used in the preparation of cyanogen. **Mercuric thiocyanate** $\text{Hg}(\text{CNS})_2$ is formed as a white precipitate on adding KCNS to $\text{Hg}(\text{NO}_3)_2$ solution; when made into small pills with gum tragacanth soaked in water, and lit with a taper it gives poisonous fumes of mercury and a long, snake-like mass of a polymerised cyanogen product (*Pharaoh's serpent*).

Mercuric fulminate $\text{Hg}(\text{ONC})_2$ (isomeric with the cyanate) is obtained as a white precipitate on warming a solution of mercury in excess of nitric acid with alcohol. It is used in making detonators, since it explodes on percussion. It is being replaced to some extent by lead azide $\text{Pb}(\text{N}_3)_2$.

By adding a solution of HgI_2 in liquid ammonia to an excess of potassium KNH_2 dissolved in liquid ammonia, a chocolate-brown precipitate of **mercuric nitride** Hg_3N_2 is formed. **Mercuric acetylide** $3\text{C}_2\text{Hg}, \text{H}_2\text{O}$ is formed as a white precipitate on passing acetylene into a solution of mercuric oxide in ammonia and ammonium carbonate.

Mercuramine compounds. - The tendency to form complex compounds is very marked in the case of mercury. By the action of ammonia gas on mercuric chloride a compound $\text{HgCl}_2 \cdot 2\text{NH}_3$, called *fusible white precipitate*, is obtained. This is also formed as a white precipitate by adding a solution of mercuric chloride to a boiling solution of ammonium chloride and ammonia. It was formerly regarded as mercuri-diammonium chloride $\text{Hg}(\text{NH}_3)_2$, but is probably an additive compound $[\text{Hg}(\text{NH}_3)_2]_2\text{Cl}_2$. If ammonia is added to a solution of mercuric chloride, mercuric oxide is not obtained, but a white precipitate of **aminomercuric chloride** $\text{NH}_2 \cdot \text{HgCl}$, i.e. mercuric chloride in which one atom of chlorine is replaced by the amino-group NH_2 , is formed. This is called *infusible white precipitate*.

If mercuric oxide is gently warmed with aqueous ammonia, a yellow powder known as **Millon's base** is formed. According to Rammeisberg (1888) this is the hydroxide corresponding with the dimercuriammonium hydroxide $\text{NHg}_2 \cdot \text{OH} \cdot 2\text{H}_2\text{O}$. On drying at 125° in ammonia gas, dark-

brown explosive $\text{NHg}_2 \cdot \text{OH}$, or perhaps $\text{O} \begin{array}{l} \diagup \text{Hg} \\ \diagdown \text{Hg} \end{array} \text{NH}$, is formed. Hofmann

and Marburg (1899) formulated Millon's base as $(\text{HOHg})_2\text{NH}_2 \cdot \text{OH}$, but the formula $\text{HO} \cdot (\text{Hg}_2\text{O}) \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$ is now adopted, since it loses H_2O when dried in ammonia gas and forms $\text{HO} \cdot \text{Hg} \cdot \text{O} \cdot \text{Hg} \cdot \text{NH}_2$. Compounds isomeric with the salts of Millon's base were prepared by Franklin by the action of liquid ammonia on HgBr_2 and HgI_2 ; he regarded them as $\text{Hg} : \text{N} \cdot \text{HgX}$ and formulated Millon's base as $\text{HO} \cdot \text{Hg} \cdot \text{NH} \cdot \text{Hg} \cdot \text{OH}$.

By the action of aqueous ammonia on calomel a black powder is formed, which is a mixture of infusible white precipitate and finely-divided mercury, $\text{Hg} + \text{NH}_3 \cdot \text{HgCl}$. A similar black precipitate is formed by adding ammonia to a solution of mercurous nitrate, $\text{Hg} + \text{NH}_3 \cdot \text{HgNO}_3$.

The formation of this black powder from calomel is said to be the origin of the name of the latter, from the Greek *kalomelas*, beautiful black,

Only mercuric salts form ammines (addition compounds with ammonia) mercurous compounds are decomposed into mercuric compounds and mercury.

CHAPTER XL

VOLTAIC CELLS

Electrical energy.—Electrolysis is accompanied by an absorption of energy. In batteries, chemical reactions occur and chemical energy is transformed into electrical energy, the inverse of electrolysis. H. E. Armstrong supposed that *all* chemical changes are really cases of reversed electrolysis, but the only changes which can furnish electric currents are those involving electrically charged ions.

In chemical reactions there is usually an evolution of heat, derived from the diminution of chemical energy. The heat evolved in a reaction at constant volume is a measure of the decrease of total energy (p. 279). If the reaction takes place so as to produce an electric current, the energy of the current is a measure of the decrease of free energy in the reaction, since it may be wholly converted into useful work by means of an electric motor.

The free energy change is the correct measure of the affinity of the reaction. The possibility of the measurement of chemical affinity in terms of electromotive force was clearly pointed out by Davy.

Although Faraday's second law shows that the same quantity of electricity (96,500 coulombs) is required in the decomposition of one gram-equivalent of a compound into its uncharged ions, the amounts of electrical work spent in the decomposition of various compounds are very different.

The energy of an electric current is given by the product of the quantity of electricity transported by the current and the electrical pressure which drives the electrons. The electrical pressure is called **electromotive force** (E.M.F.), measured in volts. The electrical energy measured in joules is given by:

$$\text{Volts} \times \text{Coulombs} = \text{Joules.}$$

The work done per second, or the **power**, is measured by the product of the amperes and volts: the unit of power, 1 joule per second, is called a watt:

$$\text{Volts} \times \text{Amperes} = \text{Watts.}$$

The watt is a small unit, so that in practice the kilowatt, or 1000 watts, is used. Energy is then measured in kilowatt hours (K.W.H.), or the number of kilowatts expended per hour.

Voltaic cells.—An arrangement in which the energy of a chemical reaction is converted into electrical energy is called a voltaic cell, since the first representative of this type of apparatus was invented by Volta in 1800.

Volta's cell consisted of a plate of zinc and one of copper immersed in dilute sulphuric acid. When the plates outside the liquid are joined by a wire the zinc dissolves, but hydrogen bubbles are evolved from the copper, not from the zinc. An electric current, recognised by its heating and magnetic effects, flows through the wire. Positive electricity passes

inside the cell from the zinc to the copper by positive hydrogen ions moving in this direction. The hydrogen ions deposit on the copper plate, give up their charges, and appear as gaseous hydrogen. The discharge is due to removal of free electrons from the copper plate : $H^+ + e = H$.

The negative charge taken from the copper is maintained by a current of electrons flowing along the wire from the zinc to the copper, *i.e.* in the opposite direction to the conventional positive current. The electrons come from the zinc, which dissolves as positively charged zinc ions : $Zn = Zn^{++} + 2e$.

If the zinc had merely dissolved in the acid without producing current the hydrogen ions would have been discharged in contact with the metal and hydrogen gas evolved from the zinc. In the cell, the hydrogen ions travel through the liquid to the copper plate in order to pick up electrons. The two reactions, when they are compelled to take place at two different places, produce a current. The reaction in a cell has, therefore, been called "chemical action at a distance."

The voltaic cell does not generate *electricity*. The electrical charges are present in the materials of the cell in the form of electrons, and the electrons are added to, or subtracted from, atoms to form ions. During this transfer of electricity, *energy* may be taken from the battery.

The Daniell cell.—The E.M.F. of the Volta cell rapidly decreases when current is taken from it, owing to deposition of hydrogen on the copper, leading to polarisation. In the Daniell cell (1836), the voltage remains practically constant. This cell consists (Fig. 374) of a rod of amalgamated zinc immersed in dilute sulphuric acid, and an outer copper vessel containing copper sulphate solution. The two solutions are separated by a pot of unglazed earthenware, which prevents them from mixing but permits the passage of ions moving from one liquid to the other.

The zinc dissolves in the dilute acid as zinc ions and the hydrogen ions passing from the liquid round the zinc through the porous partition remain in the copper sulphate solution. Instead of hydrogen ions being deposited, copper ions, more easily discharged, give up their charges to, and form a coating of copper on, the copper plate.

The net reaction is the transfer of two unit positive charges from the copper ions to metallic zinc, whereby metallic copper and zinc ions are formed : $Cu^{++} + Zn = Cu + Zn^{++}$. Since the reaction involves the transfer of $2 \times 96,500$ coulombs, and the voltage of the cell is 1.1, the decrease of free energy in the reaction is $1.1 \times 2 \times 96,500 = 212,300$ joules, or $212,300/4.184 = 50,741$ g. cal. The heat evolved in the displacement of copper from a solution of copper sulphate by zinc : $Zn + CuSO_4 = ZnSO_4 + Cu$, or $Zn + Cu^{++} = Zn^{++} + Cu$, is 50,100 g. cal. In this case, therefore, the free energy change

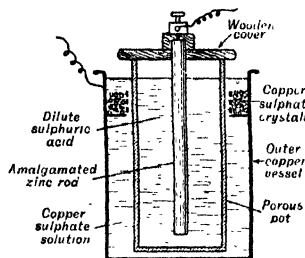


FIG. 374.—Daniell cell.

about the same as the total energy change. This is exceptional; in most cells the two are different, and may even differ in sign.

Zinc in a solution of zinc sulphate, and copper in a solution of copper sulphate, separated by a porous cell, will also give a current and may be considered as a modification of the Daniell cell. In this case the ion SO_4^{--} migrates from the CuSO_4 to the ZnSO_4 solution. Copper is deposited from the first solution, and zinc dissolves in the second.

If an external voltage slightly greater than 1.1 volts is applied to the terminals of this cell in the opposite direction to the E.M.F. of the cell, the chemical reactions are reversed. Zinc is deposited and copper dissolves. A cell of this type is called a reversible cell.

Electrode potentials.—If the zinc is replaced in the Daniell cell by cadmium, the E.M.F. changes. If silver in silver sulphate solution is substituted for copper in copper sulphate, there is also a change in E.M.F. *The voltage of a cell depends on the nature of both its electrodes, metals and solutions, and the voltage is the algebraic difference of two single potentials, one corresponding with each electrode.* These are called **electrode potentials**.

Electrolytic solution pressure.—The source of the electrode potentials may be explained by Nernst's theory of electrolytic solution pressure. A bar of zinc in a solution of zinc sulphate tends to throw off zinc ions owing to its solution pressure. But the zinc ions in the solution exert an osmotic pressure, and tend to redeposit on the metal. As a result of the first change, the metal acquires a negative charge, and the solution a positive charge. This reaction is brought to a standstill by the attraction of the opposite charges, so that a layer of positive zinc ions is attracted to the surface of the negative zinc plate (Fig. 375).

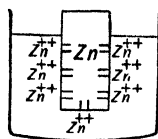


FIG. 375.—Diagram illustrating formation of an electrical double layer.

The more zinc ions are in the solution, the greater is their tendency to deposit on the metal, so that the solution pressure of the metal is opposed and finally balanced by the osmotic pressure of the ions in solution.

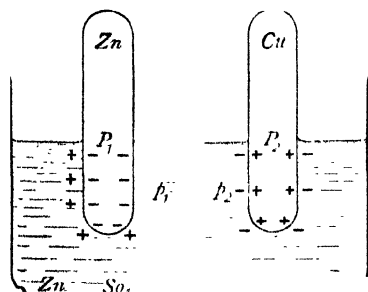


FIG. 376.—Theory of the action of a voltaic cell.

If a bar of copper is placed in copper sulphate solution the copper ions (since their osmotic pressure is opposed by a relatively small solution pressure) tend to deposit on the metal, giving up their charges. The metal becomes charged positively, leaving the solution negatively charged, but the formation of a layer of negative ions on the metal surface again puts a stop to this reaction.

If the two single electrodes, zinc and copper, are put in communication by a porous partition between the solutions, as in Fig. 376, we have a Daniell cell.

The single potentials of metals in solutions of their ions containing 1 gm. mol. per litre are given in the table below. The sign attached is that of the charge of the *electrode*. The table is called the **electromotive series**. Hydrogen dissolved in platinum or palladium acts like a metal electrode to solutions of acids, containing H^+ ions. Each entry gives the potential difference in volts at 18° between the given electrode and the hydrogen electrode in a solution normal in H^+ ions. The "absolute" potential difference between the hydrogen electrode and a normal solution of H^+ ions is about 0.274 volt, and the absolute potential of an electrode, referred to the solution at zero potential, is given by adding 0.274 to the figure in the table.

Electromotive series of the metals.

K - 2.92	Fe(Fe') - 0.44	H 0.00
Ca - 2.87	Cd - 0.40	Cu(Cu'') + 0.345
Mg - 1.05	Tl - 0.33	Hg(Hg_2'') + 0.80
Mn - 1.05	Sn(Sn'') - 0.14	Pd + 0.82
Zn - 0.76	Pb - 0.126	Ag + 0.80

The voltage of the Daniell cell with molar solutions is $0.345 - (-0.76) - 1.105$, the copper being positive.

Since ionisation takes place by addition of positive charge, one metal will dissolve in a solution of a second metal, displacing the second metal, when the electrode potential of the first metal is algebraically smaller.

Zinc in a solution of cadmium ions will dissolve and cadmium be deposited, since $-0.76 - (-0.40) = -0.36$; whilst cadmium will deposit copper, since $-0.40 - (+0.345) = -0.745$. Silver will not deposit copper from a solution of copper ions, since $0.80 - (+0.345) = +0.455$. The electromotive series is also an **affinity series**.

Although non-metals are non-conductors, their electrode potentials relative to solutions of their ions may be measured by absorbing a trace of the substance in a platinum plate, and using this as an electrode. A platinum plate immersed partly in chlorine gas and partly in a solution containing chloride ions acts as a positive chlorine electrode: $Cl_2 + 2e \rightleftharpoons 2Cl'$.

Electromotive series of non-metals.

I + 0.54	Br + 1.07	Cl + 1.36
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Thus, the voltage of the cell: $Zn | MZnSO_4 | NKBr | Br_2, Pt$ will be $1.07 - (-0.76) = 1.83$. The small potential difference between the two solutions is neglected in the above calculations. The potential between solutions containing H^+ or OH' ions is relatively large.

Decomposition of potentials.—It has been stated (p. 241) that a definite potential difference between the electrodes is required in the decomposition of an electrolyte. When the decomposition is reversible, the decomposition potential is equal to the algebraic difference of the electrode potentials of the two ions, since the electromotive force of polarisation set up by the products of decomposition, acting as a cell, must be overcome before further deposition of ions can occur.

Although some ions, such as copper and other (but not all) metal ions, are deposited by the application of the reversible decomposition potential, others and notably hydrogen ions require a larger potential than this and the excess is called the *overvoltage* (or *overpotential*) of the ion. For hydrogen this is very small on platinised platinum but is large on amalgamated lead or on mercury used as the cathode. This explains why sodium is deposited rather than hydrogen on the mercury in the Castner-Kellner cell (p. 205).

Concentration cells.—Since electrode potential depends on the concentration of the ions, two portions of the same metal immersed in two solutions of the same electrolyte of different concentrations can form a cell, known as a concentration cell. The voltage depends on the greater tendency of copper ions, *e.g.*, in concentrated solution to deposit on copper, on account of the greater osmotic pressure, than copper ions in dilute solution. The copper in the concentrated solution has a greater positive potential than that in the dilute solution. The metal dissolves in the dilute solution and deposits from the concentrated solution, until both solutions become equally concentrated. The combination then shows no E.M.F.

On a concentrated solution of stannous chloride (which must not contain much free hydrochloric acid) in a test-tube pour carefully a dilute solution of the same salt. Insert a stick of tin, (Fig. 377). After a few hours a crystalline deposit of tin forms on the rod in the concentrated solution.

If electrodes are immersed in solutions not of molar concentration with respect to the ions, a correction must be applied to the electrode potentials to take account of the influence of ionic concentration. In more concentrated solutions the osmotic pressure of the ion is more active in tending to cause deposition on the electrodes. If e_c and e_0 are the electrode potentials in solutions of ions of concentrations c and 1 gm. mol. per litre, respectively, at 18°, then :

$$e_c = e_0 + \frac{0.058}{n} \log c,$$

where n is the valency of the ion. The electrode potential of Zn in decimolar solution of ions is $-0.76 - 0.058/2 = -0.789$ volt. It is numerically greater than in molar solution, since the opposing osmotic pressure of the ions is less. The corresponding value for copper is $+0.345 - 0.058/2 = +0.316$.

If potassium cyanide is added to the copper sulphate solution in the Daniell cell, the copper ions are nearly all removed to form complex ions $\text{Cu}(\text{CN})_4'''$, and the direction of the current changes sign. On account of the low osmotic pressure of copper ions, copper dissolves and zinc ions are driven out of solution as metallic zinc.

Oxidation and reduction.—The oxidation of stannous chloride to stannic chloride, or ferrous chloride to ferric chloride, by means of



FIG. 377.—Experiment illustrating the action of a concentration cell.

chlorine, may furnish an electric current. A cell is made up as follows :

Positive pole : a platinum plate in a solution of sodium chloride, saturated with chlorine.

Negative pole : a platinum plate immersed in a solution of stannous chloride.

The two are separated by a porous partition. Chlorine dissolves in the platinum and sends off chloride ions into the solution, leaving the plate with a positive charge: $\text{Cl} + \text{e} = \text{Cl}'$. To neutralise this, negative electrons pass round the wire from the other plate, and the stannous ions which come in contact with this lose negative charges and are oxidised to stannic ions: $\text{Sn}'' - 2\text{e} = \text{Sn}''''$. The current is completed in the cell by chloride ions moving through the porous partition.

Let a cell be constructed as follows :

Negative pole : a platinum plate charged with hydrogen immersed in dilute acid.

Positive pole : a platinum plate in a solution of ferric chloride.

Hydrogen dissolved in the negative plate throws off hydrogen ions into the solution, leaving the plate charged negatively: $\text{H} = \text{H}' + \text{e}$. The negative charge passes to the other plate, and discharges Fe''' ions touching the plate to Fe'' ions: $\text{Fe}''' + \text{e} = \text{Fe}''$. This is a process of reduction.

Measurement of the E.M.F. of cells of this kind gives a measure of the relative strength of an oxidising or reducing agent, the hydrogen electrode being used as a standard.

CHAPTER XLI

GROUP III METALS

GROUP III of the periodic table is in two parts :

The (a) Sub-group : metals of the rare earths and the radioactive element actinium (p. 401).

The densities at room temperature and the lattice types of the rare earth elements and the approximate m. pts., when known, are given (c.p. = close packed ; f.c. = face-centred ; b.c. = body-centred) :

At. no.	Lattice	Density	At. vol.	M. pt.	At. no.	Lattice	Density	At. vol.	
21	Sc- α	hexag. c.p.	3.02	14.9	1200°	64 Gd	hexag. c.p.	7.95	19.7
	Sc- β	cubic f.c.	3.20	14.1		65 Tb	hexag. c.p.	8.33	19.1
39	Y	hexag. c.p.	4.34	20.5	1475°	66 Dy	hexag. c.p.	8.56	18.9
57	La- α	hexag. c.p.	5.19	22.5	810°	67 Ho			
	La- β	cubic f.c.	5.18			68 Er	hexag. c.p.	9.16	18.2
58	Ce- α	hexag. c.p.	5.78	23.2	630	69 Tm	hexag. c.p.	9.35	18.1
	Ce- β	cubic f.c.	5.81			70 Yb	cubic f.c.	7.01	24.7
59	Pr- α	hexag. c.p.	5.78	20.8	940	71 Lu	hexag. c.p.	9.74	18.0
	Pr- β	cubic f.c.	6.81						
60	Nd	hexag. c.p.	7.00	20.6	840°				
61	Pm								
62	Sm			20.0	1350°				
63	Eu	cubic b.c.		31.9					

The abnormally high atomic volumes of europium and ytterbium are noteworthy.

The electron configurations of the atoms are given on p. 822.

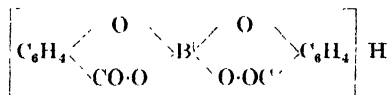
The (b) Sub-group : boron, aluminium, gallium, indium and thallium.

	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electron configuration	2.3	2.8.3	2.8.18.3	2.8.18.18.3	2.8.18.32.3
Density	2.34	2.70	5.9	7.31	11.85
Atomic volume	4.62	10.0	11.8	15.1	17.2
Melting point	2300°	659.8°	29.75°	155.4°	303.5°
Boiling point	2550°	> 2200°	> 2000°	> 1450°	1475°

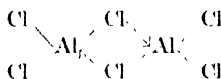
The typical group valency is 3 but boron forms several hydrides in which its valency is anomalous (p. 655) ; some metals of the rare earths (Sm, Eu, Yb) can be bivalent as well as trivalent, and in many of its stable compounds cerium is quadrivalent, as is praseodymium in

the oxide PrO_2 ; gallium and indium also form compounds in which they are uni- and (possibly) bivalent, and thallium is most stable in its univalent compounds.

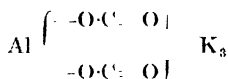
The maximum covalency of boron (in a short period) is 4, shown in many compounds, *e.g.* KBF_4 . The valency arrangement is tetrahedral in such compounds as borosalicylic acid, which show optical isomerism (Böseken, 1926):



Aluminium shows a covalency of 4 in the bimolecular halides:



and in many coordination compounds, *e.g.* $\text{Na}[\text{AlCl}_4]$, $[\text{AlCl}_3(\text{NH}_3)]$, $[\text{AlCl}_3(\text{PH}_3)]$, etc., and as it belongs to a long period it also shows a covalency of 6 in many compounds, *e.g.* $\text{Na}_3[\text{AlF}_6]$, $[\text{Al}(\text{NH}_3)_6]\text{Cl}_3$, etc., when the valency arrangement is octahedral. This is shown by the optical activity of the complex oxalate (Wahl and Andersin, 1927):



and similar compounds. The rare earth metals show a maximum covalency of 6.

The rare earths (except scandium oxide) are strongly basic oxides; boron trioxide B_2O_3 is weakly acidic and aluminium oxide weakly basic, but both are amphoteric, as are the oxides of the other elements of the *b* sub-group, except thallium. Boron forms several volatile hydrides, gallium forms a volatile Ga_2H_6 , aluminium a non-volatile AlH_3 , and solid hydrides of rare earth elements are described.

The small atomic volumes and the large charges on B^{+++} and Al^{+++} lead to the formation of covalent compounds, and the trihalides of the *b* sub-group except thallium are volatile: aluminium chloride in the vapour (except at higher temperatures) exists as Al_2Cl_6 , and GaCl_3 is also largely associated to (Ga_2Cl_6) in the vapour. The trihalides are hydrolysed by water. The rare earth chlorides MCl_3 are salt-like, not readily volatile, and not hydrolysed. All the elements (even boron) form oxy-salts such as sulphates, but carbonates are formed only by rare earths, indium, and univalent thallium.

Corresponding salts of metals of the two sub-groups are not usually isomorphous and crystallise with different numbers of molecules of water. The sulphates of metals of the *b* sub-group (except thallium sulphate) form alums $\text{Me}^I\text{Me}^{III}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, those of the *a* sub-group

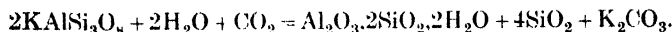
form double sulphates $Me^I Me^{III}(SO_4)_2 \cdot 8H_2O$ of a different type. Aluminium is stable in air because of a thin protective oxide film; the rare earth metals and indium are also stable in air, gallium oxidises only slightly but thallium readily in moist air. The rare earth metals oxidise on heating in air.

Organo-metallic compounds are formed by all the elements of the (b) sub-group, but not by the rare earths.

ALUMINIUM

History. Alum (from which the element aluminium takes its name) was known in very early times. Pott (1746) showed that it is derived from a peculiar earth *alumina*, which Marggraf (1754) isolated from clay. That *alumina* is the oxide of a metal was proved by Davy (1808), who isolated the impure metal which he called *aluminium*. A purer metal was obtained by Oersted (1824) by heating the amalgam obtained by the action of potassium amalgam on aluminium chloride. The pure metal was obtained by Wöhler in 1827 by the action of potassium on the chloride $AlCl_3$. Bunsen (1854) prepared it by electrolysis but the first industrial method of preparation, due to Deville (1854), depended on the reduction of sodium aluminium chloride $NaAlCl_4$ by sodium. In 1886 the production of aluminium by the electrolysis of alumina dissolved in fused cryolite was started simultaneously by Héroult in France and Hall in America.

Occurrence.—Aluminium occurs in almost all *silicate rocks* (felspar, augite, hornblende, chlorite, tourmaline and micas) and in the secondary formations *clay* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and *slate* (clay hardened and laminated by pressure). The oxide Al_2O_3 is found either anhydrous as *corundum*, or hydrated as *diaspore* $Al_2O_3 \cdot H_2O$, *gibbsite* $Al_2O_3 \cdot 3H_2O$ and *bauxite*, a mixture of diaspore and gibbsite in varying proportions. *Spinel* is $MgAl_2O_4$. *Felspar* $KAlSi_3O_8$ or $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ is a constituent of primary rocks such as granite, and by their disintegration by the combined action of moisture and atmospheric carbon dioxide soluble alkali salts and insoluble hydrated aluminium silicate (clay) are formed:

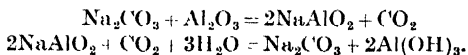


The quartz crystals and mica scales remain with the fine deposit of clay or *kaolin*, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Any iron in the rock is oxidised to ferric oxide, which colours the clay yellow or red. The kaolin may be separated from the quartz by washing, when the fine particles of clay are carried away from the larger pieces of quartz. A pure clay which has been transported by water and is more plastic than kaolin or china clay is called *ball clay*.

Common clay is contaminated with limestone, quartz and oxide of iron; a mixture of clay and limestone is *marl*, a mixture of clay and sand is *loam*. Aluminium compounds are not absorbed (except in traces) from soils by plants with the exception of mosses, the ash of which is rich in alumina. Nearly all clay contains some titanium dioxide TiO_2 . *Cryolite* Na_3AlF_6 is a semi-transparent mineral found only in Greenland.

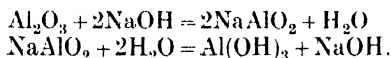
Metallurgy of aluminium.—It is not yet possible to produce aluminium from clay; the source of the metal is *bauxite*, but since this contains iron oxide and silica it is first purified to obtain pure alumina.

In the old process bauxite is heated to redness with sodium carbonate, when sodium aluminate NaAlO_2 is produced, alumina being a feebly acidic oxide. The mass is treated with water, forming finely divided oxide of iron which can be used for the purification of coal gas (p. 613) and a solution of sodium aluminate, from which a granular precipitate of aluminium hydroxide is thrown down by carbon dioxide:



On igniting the precipitate, Al_2O_3 is obtained and the solution of Na_2CO_3 is evaporated and used again.

The British Aluminium Co. at Larnie (Ireland) uses the *Bayer process*. The calcined bauxite is digested with caustic soda solution under pressure, giving a solution of sodium aluminate and leaving oxide of iron which cannot be used for any purpose. The solution of sodium aluminate (with some sodium silicate) is agitated with precipitated alumina, when nearly all the aluminium in solution is thrown out as a sandy precipitate of β -alumina (which contains some sodium), which is easily washed and on calcination yields nearly pure alumina:



The alumina is then dissolved in fused cryolite (now usually artificial) and electrolysed with carbon electrodes.

The electric furnace consists of an iron box lined with blocks of carbon and made the cathode. The anodes are carbon rods set in a row (Fig. 378) about 2 to 3 in. above the bottom of the trough. The temperature is over 900° .

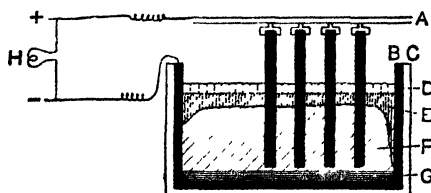


FIG. 378.—Electric furnace for aluminium: A, carbon anodes; B, carbon lining; C, cast-iron vessel; D, solid alumina; E, crust of solidified electrolyte; F, molten electrolyte; G, molten metal; H, low voltage charge control lamp.

The alumina is electrolysed: the liquid aluminium forms a pool below the anodes and the oxygen liberated burns the anodes to CO and CO_2 in about equal volumes. The charge is covered with solid alumina and fresh alumina is added from time to time to replace that decomposed.

The decomposition is indicated by a rise in resistance, the shunted lamp brightening. The metal has a purity of 99 per cent Al, the impurities being chiefly iron and silicon.

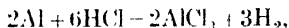
Pure aluminium (99.98 per cent) is made by the *Hoopes' process*. A liquid aluminium-copper alloy anode is covered with fused cryolite and

barium fluoride, floating on which is a cathode of pure molten aluminium. The very pure metal differs in many properties from the 99 per cent metal.

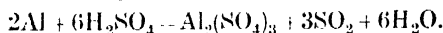
Properties.—Aluminium is silver-white when pure, but usually has a blue tinge. It is very ductile and malleable. On account of its small density it is used in construction work. It has a high tensile strength but is rather soft. The alloy of aluminium and magnesium is still lighter and can be worked easily in a lathe, whilst an alloy of aluminium, copper, magnesium and manganese, can be worked hot or cold and hardened by quenching in water, the hardness being increased by tempering after quenching. Alloys of aluminium with copper are called *aluminium bronzes*.

Aluminium is unchanged in pure dry air, a thin transparent protecting film of oxide being formed, but it corrodes in impure air. The film is removed by rubbing the metal with moist mercuric chloride, producing a liquid amalgam to which the oxide cannot adhere, and rapid oxidation occurs forming moss-like excrescences of oxide. Amalgamated aluminium foil is a useful reducing agent in neutral solutions. Aluminium foil or powder readily burns with a brilliant flame when heated in air. The metal is a good conductor of heat and electricity, being used for electric cables: for equal *weights* it is a better conductor than copper. The *powder* is made by stamping pieces of thin sheet in oil and really consists of thin flakes.

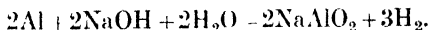
Although only superficially attacked by pure water, aluminium is attacked by sea water and solutions of some salts (*e.g.* magnesium chloride) which remove the oxide film. Dilute or cold concentrated sulphuric acid has very little action, and the *pure* metal is almost unattacked by dilute or concentrated nitric acid. Dilute and concentrated hydrochloric acid readily dissolve aluminium with evolution of hydrogen:



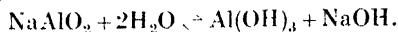
and hot concentrated sulphuric acid attacks it:



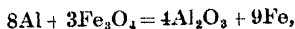
Aluminium readily dissolves in solutions of alkalis, forming **aluminates**:



These are hydrolysed in solution:



The great evolution of heat in the combination of aluminium with oxygen is utilised in Goldschmidt's *thermit process* for reducing metallic oxides (*e.g.* Cr_2O_3 , Mn_2O_3) and for the production of molten iron for welding broken articles (rails, ship's parts, etc.) *in situ*. A mixture of aluminium powder and oxide of iron ("smithy scales") is placed in a crucible and ignited by a burning magnesium wire. A violent reaction occurs:



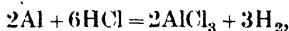
and molten iron covered with a layer of molten alumina is formed. The iron is tapped from below directly on to the joint to be welded, enclosed in a mould of fire-clay and sand.

ALUMINIUM COMPOUNDS

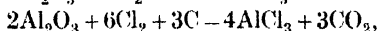
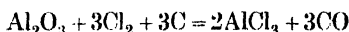
Halogen compounds.—Compounds of aluminium with all the halogens are known.

Aluminium fluoride AlF_3 is insoluble in water although aluminium dissolves in hydrofluoric acid; the fluoride is obtained in crystals by evaporating the solution. It is not decomposed by alkali solutions but only on fusion with sodium carbonate. The mineral *cryolite* is Na_3AlF_6 . An artificial cryolite is made by the reaction: $2\text{AlF}_3 + 6\text{NH}_4\text{F} + 6\text{NaNO}_3 = 2\text{Na}_3\text{AlF}_6 + 6\text{NH}_4\text{NO}_3$ in solution. Cryolite is decomposed on heating with lime: $\text{Na}_3\text{AlF}_6 + 3\text{CaO} = 3\text{CaF}_2 + \text{Na}_3\text{AlO}_3$.

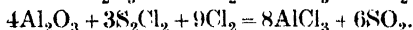
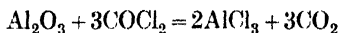
Aluminium chloride AlCl_3 is prepared anhydrous by heating aluminium in chlorine or hydrogen chloride gas:



by heating an intimate mixture of alumina and carbon in a current of dry chlorine:



and by heating alumina in a stream of carbonyl chloride or sulphur chloride vapour and chlorine:



(These are general methods for the preparation of metallic chlorides). Aluminium oxide alone is *slowly* decomposed when strongly heated in chlorine, oxygen being evolved.

In the laboratory, 10 gm. of aluminium turnings are heated in a hard glass tube connected with a bottle (Fig. 379) and a rapid current of chlorine

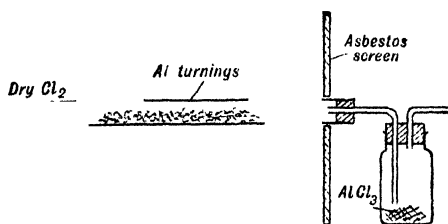


FIG. 379.—Preparation of aluminium chloride.

dried by sulphuric acid is passed over the metal. A sublimate of aluminium chloride is formed.

Crude aluminium chloride is now largely used in petroleum "cracking" and is made by passing chlorine over a heated mixture of bauxite and carbon.

Anhydrous aluminium chloride is a white crystalline very hygroscopic substance (usually coloured yellow by ferric chloride as impurity) which fumes in moist air. On heating it sublimes at 183° without pre-

vious fusion (m. pt. under 2 atm. pressure 193°). The vapour density at 350° corresponds approximately with Al_2Cl_6 but rapidly falls with rise of temperature, until at 750° it corresponds with $AlCl_3$, then remaining constant at higher temperatures: $Al_2Cl_6 \rightleftharpoons 2AlCl_3$. In organic solvents the formula is $AlCl_3$. Its ready volatility and solubility in organic solvents show that aluminium chloride resembles a covalent compound (e.g. BCl_3) rather than a salt, but when fused it is an electrolyte.

With a little water aluminium chloride forms a crystalline hydrate $AlCl_3 \cdot 6H_2O$, more conveniently prepared by dissolving aluminium or soluble alumina in concentrated hydrochloric acid and saturating the solution with hydrogen chloride gas. Aluminium chloride is hydrolysed in solution: $AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl$, which can be titrated with alkali as if it were free hydrochloric acid. The compound $NaAlCl_4$ is formed when aluminium chloride and sodium chloride are heated in a sealed tube.

Aluminium bromide $AlBr_3$ (m. pt. 93°, b. pt. 263°) is prepared similarly to the chloride and has similar properties; it forms a crystal hydrate $AlBr_3 \cdot 6H_2O$.

Aluminium iodide AlI_3 (m. pt. 185°, b. pt. 350°) is formed by heating aluminium and iodine in a sealed tube, or by acting on aluminium with iodine dissolved in carbon disulphide. It forms a crystal hydrate $AlI_3 \cdot 6H_2O$. Aluminium iodide when heated with carbon tetrachloride forms carbon tetraiodide:



Aluminium bromide and iodide in the vapour state have the formulae Al_2Br_6 and Al_2I_6 , but dissociate on heating.

Aluminium oxide.—Aluminium oxide or *alumina* Al_2O_3 occurs as *corundum* in rhombohedral crystals nearly as hard as diamond; *emery* is an impure fine-grained variety used in grinding and polishing. Corundum when transparent forms a number of gems: *oriental topaz* (yellow), *sapphire* (blue, due to cobalt or titanium oxides), *ruby* (red, due to chromium oxide), *oriental amethyst* (violet, due to manganese oxide), *oriental emerald* (green). (The true emerald is beryllium aluminium silicate.) There are two forms of aluminium oxide, stable α - Al_2O_3 (corundum, hexagonal-rhombohedral), and γ - Al_2O_3 (cubic stable below 1000°).

Artificial rubies are produced by dropping powdered alumina containing chromium sesquioxide through the centre of an oxyhydrogen flame. The fused mass ("boule") is caught on a rod of alumina; it is not amorphous but forms a single crystal which may be cut. *Artificial sapphires* are made with alumina to which Fe_3O_4 and TiO_2 are added and a reducing flame is used.

* *Artificial corundum*, used as a refractory and abrasive, is prepared by fusing *bauxite* in the electric arc furnace, allowing the impurities to settle,

cooling, and crushing the upper part. The powder is mixed with a little clay and felspar, moulded, dried and fired in a porcelain kiln. It differs from silica in being a *basic* refractory.

Bauxite cement (*ciment fondu*) is made by fusing nearly equal weights of bauxite and lime. The clinker is finely ground. This cement, unlike ordinary cement, resists the action of sea water.

Aluminium hydroxide.—On adding an alkali to a solution of an aluminium salt, *e.g.* alum, a white gelatinous precipitate of aluminium hydroxide is produced, soluble in excess of sodium or potassium hydroxide (forming aluminates) but almost insoluble in dilute ammonia. It is amorphous and dries to a glassy solid.

On heating the hydroxide to dull redness it loses water and forms a white powder of alumina. This is also formed by heating ammonia alum (p. 816). If it has not been strongly heated the alumina is soluble in acids, but when ignited it becomes denser and insoluble in acids and can be brought into solution only by fusing with sodium hydroxide (forming sodium aluminate) or potassium hydrogen sulphate (forming aluminium sulphate).

Apparently some kind of crystalline rearrangement occurs on heating, and other oxides, *e.g.* Cr_2O_3 , Fe_2O_3 , MgO , TiO_2 , undergo more or less sudden exothermic changes at higher temperatures, increasing in density and becoming insoluble in acids and generally less reactive. In the case of zirconia, ZrO_2 , especially, but to a less extent with some of the other oxides, the change is accompanied by incandescence. These changes were observed by Berzelius.

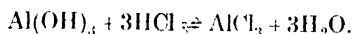
Several definite hydrates of alumina exist, characterised as α and γ according as they give on dehydration $\alpha\text{-Al}_2\text{O}_3$, the hexagonal-rhombohedral corundum, or $\gamma\text{-Al}_2\text{O}_3$, a cubic form stable below 1000° . *Diaspore*, found as a mineral, is $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and breaks up into $\alpha\text{-Al}_2\text{O}_3$ and water in steam at 400° . *Böhmite*, $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, is precipitated from boiling solution by ammonia and also occurs in bauxite from Les Baux: it is the first product of the ageing of an amorphous gel and is stable in steam at 400° . *Gibbsite*, the most stable form of trihydrate, $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is found as a mineral and is formed from bayerite by long shaking with not too dilute alkali at 60° . *Bayerite*, $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, produced from böhmite gel by ageing under dilute alkali, is metastable at room temperature with respect to gibbsite, but is stable with respect to böhmite. The compounds (the identity of which is confirmed by X-ray spectral appear to be true hydroxides: diaspore and böhmite, $\text{O}=\text{Al}(\text{OH})$, gibbsite and bayerite, $\text{Al}(\text{OH})_3$ (Lehl, 1936).

Precipitated aluminium hydroxide readily adsorbs colours and colloidal substances. Hence alum and aluminium salts are largely used as *mordants* in dyeing and for clarifying water and liquids such as sewage. In mordanting the alumina is first precipitated in the fabric and the latter dipped into the solution of the dye. In clarification lime-water is added to precipitate

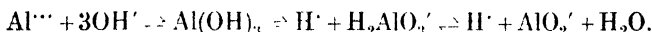
alumina. Fabrics are waterproofed by steeping in a solution of aluminium acetate and steaming, when colloidal alumina is precipitated in the pores.

Colloidal aluminium hydroxide is known in two forms. (a) A solution of the precipitated hydroxide in aluminium chloride solution gives on dialysis a colloidal solution which acts as a mordant, forms lakes with dyes, and is coagulated by alkalis and salts, the precipitate being soluble in acids (Graham, 1861). (b) A solution of aluminium acetate kept for some time at 100°, the water which evaporates being replaced, loses all the acid and a second colloidal variety (*meta-aluminium hydroxide*) is formed, which does not form lakes or act as a mordant: it is precipitated by acids, alkalis, and salts, but the gel is sparingly soluble in acids (Crum, 1854). A milky colloidal solution is also formed by the action of 4 per cent acetic acid on the well-washed precipitated hydroxide.

Aluminium hydroxide dissolves in acids producing aluminium salts:

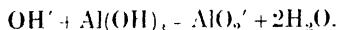


The reaction is reversible and the salts are hydrolysed by water, since aluminium hydroxide is a weak base. The hydroxide also dissolves in a solution of sodium or potassium hydroxide, producing **aluminates**, which are extensively hydrolysed by water, and it can thus act also as a weak acid. The acidic properties are weaker than the basic and they are caused by hydroxyl groups liberating hydrogen ions:

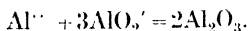


A substance having both acidic and basic functions in presence of strong bases and strong acids, respectively, is called an **amphoteric electrolyte** (or **ampholyte**). Its salts with strong acids and strong bases are hydrolysed in solution.

In solution, only *meta-aluminates*, e.g. NaAlO_2 , seem to exist, since the freezing point of a solution of sodium hydroxide is unaltered by dissolved aluminium hydroxide, so that an OH' ion is replaced by AlO_2' :



If solutions of alumina in acid and alkali, respectively, are mixed, the whole of the alumina may be precipitated:



Solutions of aluminates are so largely hydrolysed:



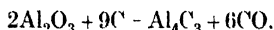
that they may be titrated with acids as if they were alkali hydroxides, and on standing the alumina is slowly deposited. When boiled with alumina, most of the aluminium hydroxide is precipitated.

The mineral *spinel* Al_2MgO_4 and related compounds, $\text{Al}_2^3+[\text{XO}_4]^{6-}$, where $\overset{\text{II}}{\text{X}} = \text{Be}$ (in *chrysoberyl*), $\overset{\text{II}}{\text{Zn}}$, $\overset{\text{II}}{\text{Fe}}$, $\overset{\text{II}}{\text{Co}}$, $\overset{\text{II}}{\text{Mn}}$, formerly regarded as aluminates,

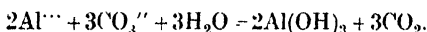
have the aluminium as cation. Al_2CoO_4 is *Thenard's blue*, obtained by heating alumina with cobalt nitrate (blow-pipe test).

Aluminium peroxide Al_2O_4 (?) mixed with alumina is precipitated by adding excess of 30 per cent H_2O_2 to alumina dissolved in 30 per cent potassium hydroxide solution (Terni, 1912).

Aluminium carbide Al_4C_3 is a yellow solid formed by heating a mixture of alumina and carbon in the electric furnace :



With water or dilute acids it evolves methane (p. 604). Aluminium carbonate does not exist, since alumina is a very weak base, and aluminium hydroxide is precipitated when a solution of alkali carbonate is added to a solution of an aluminium salt :



The basic sodium aluminium carbonate $\text{Na}(\text{AlO})\text{CO}_3 \cdot \text{H}_2\text{O}$ occurs as the mineral *dawsonite*.

Aluminium silicates and ceramics.-- Aluminium silicates are found in many minerals and in clay, used for making ceramic products (Greek, *keramos*, clay, or a pot) such as bricks, pottery and porcelain. Pure clay (*kaolinite*) $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ or $[\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2]_2 \cdot 3\text{H}_2\text{O}$, on heating loses free and combined water and shrinks, above 1000° reaction occurs with formation of the crystal form of silica called cristobalite (p. 659) and *mullite* $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; at 1500° this sinters to a stony mass which at higher temperatures softens and then fuses.

Clay used in making pottery is washed and the coarse particles allowed to settle. The fine clay deposit is mixed with ground flint or felspar and excess of water is removed by air drying. It is then highly plastic and can be worked on the wheel. The goods are air dried by stacking in warmed rooms and then fired in clay boxes called *saggars*, stacked in a kiln. The product, which has undergone shrinkage, is called *biscuit*.

The plasticity of a clay depends on the state of hydration, fineness of the particles and content of organic matter; on baking a plastic clay tends to shrink and crack, so that some non-shrinking material such as calcined clay, bone ash, or ground flint is added to prevent this. For coarse earthenware, clay only is used.

Bricks are made from impure clay containing sand and oxide of iron which gives them a red colour after firing at about 950°. The yellow bricks used in the South of England are made from mixtures of clay and chalk.

Sand-lime bricks are not made from clay but from a mixture of sand and slaked lime made to a paste with water, moulded and heated in steam at 125 lb. pressure; calcium silicate CaSiO_3 is formed and cements the sand particles together. Refractory *silica bricks* are made from crushed quartz or *ganister* (silica rock) bonded with 2 per cent of lime (see p. 662).

Purer clay is used for *earthenware* which is fired at a higher temperature than bricks: the presence of ferric oxide produces a buff-coloured or red product. *Porcelain* is made from a mixture of the purest china-clay or *kaolin* free from iron, with ground felspar and quartz. It is fired at about 900° , then the glaze is put on and the goods are fired at a bluish-white heat (1300° – 1500°). The temperature is regulated by pyrometers, or by small clay cones (*Seeger cones*) which soften and bend over at particular temperatures in the furnace. The mass undergoes partial fusion and the product is translucent. *English bone china* contains 30 to 50 per cent of bone-ash (calcium phosphate).

Clay containing much silica and alumina in comparison with basic oxides (Na_2O , CaO) is very refractory, and is called *fireclay* (e.g. Stourbridge clay). This is made into crucibles and refractory bricks and to prevent undue contraction on firing, broken firebricks ("grog") are added to the clay before heating.

The clay after firing forms the *body*, *biscuit* if porcelain clay is used, otherwise *earthenware*. The *glaze* is a glassy surface imparted to the body and intimately united with it. Earthenware drain pipes and cheaper goods are *salt-glazed*: common salt is thrown into the kiln and vaporises at the high temperature, forming a thin layer of fusible silicate on the surface of the ware. Salt-glazed ware is suitable for containing acids. Table-ware is usually *lead-glazed*: it is dipped into a creamy paste of a mixture of lead oxide, clay and ground flint. Some of this adheres to the surface and is fused in the furnace to a glass. *Porcelain glaze* is applied by dipping and re-firing at a higher temperature than in making the biscuit; the glaze may be ground felspar, quartz and kaolin. In making cheaper earthenware the glaze is put on before firing.

The ware may be *painted* before glazing or some colours are applied on the glaze; the colours are metallic oxides (e.g. cobalt oxide) which form coloured glasses with the glaze or with lead oxide and silica, or borax, mixed with the colouring oxide.

Ultramarine. The blue mineral *lapis lazuli* is a sodium aluminium silicate containing sulphur in some form not completely defined but probably as sodium sulphide. In 1826 Guimet obtained artificial *lapis lazuli* or ultramarine.

A mixture of kaolin, soda-ash or sodium sulphate, sulphur, and resin or wood charcoal is heated to redness in a closed crucible. A *white ultramarine* is formed in complete absence of air, but usually when air is admitted during heating a *green ultramarine* is formed. If this or white ultramarine is mixed with powdered sulphur and heated in air, the commercial *blue ultramarine* is formed, which is ground and washed. If this is heated in a stream of dry chlorine, nitric oxide, or hydrogen chloride, a *violet* and finally a *red, ultramarine* result.

The sodium may be replaced by the equivalent of silver by treatment with silver nitrate and a yellow *silver ultramarine* is formed. From this, by the action of potassium and lithium chlorides, potassium and lithium ultramarines are formed.

The composition of blue ultramarine was given by Hoffmann (1873) as $\text{Na}_7\text{S}_2\text{Al}_6\text{Si}_6\text{O}_{24}$. X-ray examination suggests a body-centred cubic lattice, the unit cube containing $\text{Al}_6\text{Si}_6\text{O}_{24}$. The structure contains large holes and channels accommodating sodium ions and sulphur perhaps in the form of disulphide ions $\text{S}-\text{S}''$.

Alkalis are without action on ultramarine, so that it can be used in laundering to give a white appearance to linen, as it is not attacked by soap or soda. Acids, however, rapidly decompose it forming hydrogen sulphide and a white gelatinous residue.

Aluminium nitride AlN is formed by heating aluminium powder in nitrogen at 740° ; it is decomposed by hot dilute alkali:



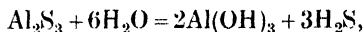
The formation of aluminium nitride by heating a mixture of bauxite and carbon in nitrogen at 1600° : $\text{Al}_2\text{O}_3 + \text{N}_2 + 3\text{C} \rightarrow 2\text{AlN} + 3\text{CO}$, and its decomposition by hot dilute alkali were proposed by Serpek for the utilisation of atmospheric nitrogen, but the process does not seem to be used.

Aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is a deliquescent salt prepared by dissolving precipitated aluminium hydroxide in dilute nitric acid, evaporating and crystallising. It decomposes on heating, alumina being formed. It is used as a mordant and for adding to thorium oxide in making gas mantles.

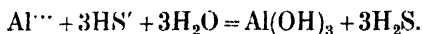
Aluminium phosphide AlP is formed by heating aluminium powder and red phosphorus; it is decomposed by water with evolution of phosphine.

Aluminium phosphate AlPO_4 is formed as a gelatinous precipitate by adding a neutral solution of an aluminium salt to sodium phosphate solution; it is soluble in mineral acids, alkalis and ammonia. A basic aluminium phosphate $(\text{AlOH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ is the mineral *wavellite*. *Turquoise* is $\text{Al}_2(\text{OH})_3\text{PO}_4 \cdot \text{H}_2\text{O}$ with part of the Al_2 replaced by Cu^{II} and Fe^{II} (causing the blue colour) and Ca^{II} .

Aluminium sulphide Al_2S_3 is formed by adding sulphur to fused aluminium, or by passing sulphur or carbon disulphide vapour over a strongly-heated mixture of alumina and carbon: $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{S} \rightarrow \text{Al}_2\text{S}_3 + 3\text{CO}$. When pure it is yellow. It is completely hydrolysed by water:

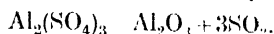


and only aluminium hydroxide is precipitated when ammonium sulphide is added to a solution of an aluminium salt:

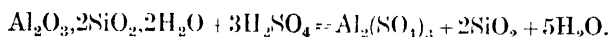


Aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ occurs native as *hair salt* or *feather alum*; basic aluminium sulphate $\text{Al}_2(\text{OH})_4\text{SO}_4 \cdot 7\text{H}_2\text{O}$ is *websterite*.

If alumina is dissolved in hot concentrated sulphuric acid, the liquid on cooling slowly deposits an indistinctly crystalline mass of hydrated aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$. This is purified by redissolving in a little water and adding alcohol, when an oily supersaturated solution separates, which soon solidifies to lustrous scaly crystals. On heating, the crystals intumescence and lose water, leaving a white mass of anhydrous aluminium sulphate, which decomposes at 800° :



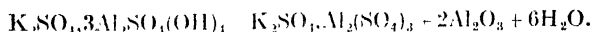
Impure aluminium sulphate is made by heating kaolin (clay) with concentrated sulphuric acid, or bauxite with diluted sulphuric acid. In the first case silica separates :



The settled solution is evaporated and the crystals pressed. The product may contain a considerable amount of ferric sulphate (especially if bauxite is used) which, although it does not form mixed crystals with aluminium sulphate, cannot be separated from it by crystallisation. The crude mixture, known as *alumino ferric*, is used for the precipitation of colloidal matter from sewage. If the ferric is reduced to a ferrous salt, say by hydrogen sulphide, the aluminium sulphate may be crystallised out alone.

Alums.—The double salts of aluminium sulphate and potassium and ammonium sulphates are common *potassium alum* $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and *ammonium alum* $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ or $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, respectively. They readily crystallise in octahedra (aluminium sulphate does not easily crystallise).

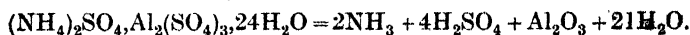
Alum is made from *alum shale*, i.e. aluminium silicate permeated by pyrites FeS_2 , which on roasting in heaps forms aluminium sulphate. The roasted shale is lixiviated (or, if necessary, boiled with sulphuric acid) and after evaporation either ammonium or potassium sulphate or chloride is added, when alum is deposited. Potash alum is prepared from *alunite* or *alum-stone* $\text{K}_2\text{SO}_4 \cdot 3\text{Al}_2\text{SO}_4(\text{OH})_4$, by roasting with fuel, exposing to air, lixiviating and crystallising :



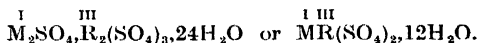
Alum is made by adding potassium or ammonium sulphate to a solution of aluminoferric. Since alum is readily purified by recrystallisation it may be obtained free from iron (which gives dull colours to lakes in mordanting) much more readily than aluminium sulphate. Alum prepared from alunite, called *Roman alum*, although pink from the presence of ferric oxide, is quite free from soluble iron.

Potassium alum when heated melts and loses the whole of its water at 200° , forming a white porous mass of *burnt alum*. Above a red heat the aluminium sulphate decomposes. Ammonium alum melts on

heating, loses ammonia and sulphuric acid and at a higher temperature leaves a residue of pure alumina :



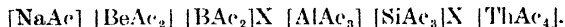
The name alum is given to all double-salts of the type



$\overset{\text{I}}{\text{M}}$ may be Li, Na, K, NH_4 , Rb, Cs, (Ag ?), Tl, hydroxylammonium (NH_4O), or the radical of a quaternary nitrogen base, such as $\text{N}(\text{CH}_3)_4$.

$\overset{\text{III}}{\text{R}}$ may be Al, Fe, Cr, Mn, Ir, Ga, In, Ti, V, Co, Rh. Rare-earths do not form alums. The selenate radical SeO_4 may replace SO_4 . The alums are not stable complex compounds, since in solution they give the ions of the component salts. All the alums are isomorphous, form mixed crystals in all proportions and also layer-crystals, i.e. a crystal of any one alum continues to grow in a solution of any other. The sodium alum is very soluble and its preparation is difficult ; lithium alum crystallises only below 0° ; rubidium and caesium alums are sparingly soluble.

An interesting compound is aluminium acetylacetonone AlAc_3 , where $\text{Ac} = -\text{O}(\text{CH}_3)\text{C} : \text{CH} : \text{C}(\text{CH}_3) : \text{O}$, which is attached by one covalent bond and one co-ordinate linkage (p. 418). It is a neutral volatile compound with the normal vapour density. Similar compounds are formed with other elements but some are salts :



The atomic weight of aluminium has been found from the ratio $\text{AlBr}_3 : 3\text{AgBr}$. The valency has been found from the atomic heat of aluminium and the vapour density of aluminium chloride above 750° , the vapour density of aluminium acetylacetonone, and the molecular weight of AlCl_3 in solution in pyridine.

GALLIUM

The rare element gallium occurs in minute traces in most specimens of zinc blende, and was discovered by the spectroscope in a blende from Pierrefitte by Lecoq de Boisbaudran in 1875. It is the *eka-aluminium* of Mendeléeff. Gallium occurs in traces in bauxite, in commercial aluminium, in the residues of zinc distillation, and in some coal ash. It is extracted from the by-products of the Mansfeld copper schists. Middlesborough cast-iron contains 1 part of gallium in 33,000. Gallium melts at 29.75° and remains supercooled, so that it is often liquid at room temperature.

Gallium forms a volatile hydride GaH_3 . The element is normally trivalent, but sometimes is apparently bivalent, as in GaCl_2 , which may be $\text{GaI}[\text{Ga}^{\text{III}}\text{Cl}_4]$, and GaS , and it is univalent in Ga_2O and Ga_2S .

Gallium trichloride GaCl_3 (associated in the vapour to Ga_2Cl_6) is made by burning the metal in chlorine, and can be extracted from solution in hydrochloric acid by ether. Alkalis precipitate a solution as gallium hydroxide $\text{Ga}(\text{OH})_3$, which is amphoteric like alumina. The white gallium oxide Ga_2O_3 is formed by burning the metal in oxygen. The yellow gallium sulphide Ga_2S_3 is formed by heating the metal in sulphur vapour and is

decomposed by water. Gallium sulphate $(Ga_2(SO_4)_3 \cdot 16H_2O)$ readily forms alums. No carbonate is known, the hydroxide being precipitated. The dark grey gallium nitride (GaN) , formed by heating the metal in ammonia gas, is stable to air, water, and dilute acids.

INDIUM

Indium was discovered by Reich and Richter (1863) in the spectroscopic examination of zinc blende from Freiberg. It gives a dark-blue flame coloration. It occurs in all commercial tin; the Bolivian mineral *cylindrite* contains 0.1-1.0 per cent. The metal is precipitated from solution by zinc and is purified electrolytically. It is soft and is not attacked by air or boiling water, and has been used for plating silver. It burns when heated in air to the yellow indium oxide In_2O_3 , which is easily reduced to the metal. Indium dissolves in cold concentrated sulphuric or hydrochloric acid, and in alkalis, with evolution of hydrogen.

Indium is normally trivalent but forms three chlorides, $InCl$, $InCl_2$ (perhaps $In^I(In^{III}Cl_4)$) and $InCl_3$. Indium trichloride is formed by burning the metal in chlorine; when heated with the metal it forms $InCl_2$ and $InCl$. The gelatinous indium hydroxide $In(OH)_3$ is precipitated by ammonia or alkali hydroxides and is soluble in excess of alkali hydroxide, but the solution soon becomes turbid. Indium sulphate $In_2(SO_4)_3$ forms alums; indium carbonate $In_2(CO_3)_3$ is precipitated, with some hydroxide, by alkali carbonate.

THALLIUM

In 1861 Crookes observed a bright-green line in the spectrum of a specimen of flue dust from a vitriol works, which he regarded as due to the presence of a new metal. The element was independently discovered, and first isolated in quantity, by Lamy in 1862. Crookes gave it the name thallium from the Greek *thallos*, a young twig, on account of the colour imparted to the flame. The only minerals rich in thallium are *crookesite* (17 per cent Tl, with Se, Cu, Ag), and *lorandite* $TlAsS_2$.

Thallium may be obtained from vitriol flue-dust or from pyrites (from which it passes into the flue-dust) by dissolving in *aqua regia*, evaporating, precipitating with hydrogen sulphide and then ammonia in the usual group separations, and then adding potassium iodide to the filtrate. A yellow precipitate of thallic iodide TlI is formed which gives a green coloration when heated on platinum wire in a Bunsen flame. If this is reduced with zinc and dilute sulphuric acid the metal is obtained. Thallic chloride $TlCl$ is reduced by fusing with sodium carbonate and potassium cyanide. Thallium is a soft greyish-white metal, m. pt. 303.5°; its vapour density corresponds with the formula Tl . It oxidises in moist air, decomposes steam at a red heat, and dissolves readily in dilute sulphuric acid and especially in nitric acid. It is less easily soluble in hydrochloric acid, since thallic chloride $TlCl$ is sparingly soluble. Thallium compounds are very poisonous and thallic sulphate has been used in exterminating ants.

Thallium forms two series of compounds: the thallic compounds TlX in which it is univalent and shows analogies with silver and the alkali-

metals, and the thallic compounds TlX_3 in which it is trivalent and has resemblances to aluminium and ferric iron. Thallous iodide TlI resembles lead iodide PbI_2 . The thallic compounds are essentially covalent.

If thallium is dissolved in dilute sulphuric acid and the solution evaporated, thallous sulphate Tl_2SO_4 , isomorphous with potassium sulphate and forming an alum $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, is obtained. From its solution hydrochloric acid precipitates white thallous chloride $TlCl$, resembling silver chloride in becoming violet on exposure to light, but differing from silver chloride in being sparingly soluble in ammonia. With chloroplatinic acid a sparingly soluble chloroplatinate Tl_2PtCl_6 , resembling K_2PtCl_6 , is formed. Iodides precipitate yellow thallous iodide TlI , almost insoluble in cold water but dissolving in 830 parts of boiling water.

Thallous hydroxide $TlOH$ is obtained in yellow needles by decomposing a solution of thallous sulphate with baryta-water, filtering, and evaporating. The solution is alkaline and turns turmeric paper brown, but then bleaches it. If heated out of contact with air at 100° $TlOH$ forms black thallous oxide Tl_2O , dissolving in water to form a colourless solution of $TlOH$.

Hydrogen sulphide gives a black precipitate of thallous sulphide Tl_2S from alkaline solutions of thallous salts. It is soluble in dilute acids (except acetic) but insoluble in ammonium sulphide. Thallous hydroxide solution absorbs carbon dioxide forming the soluble thallous carbonate, Tl_2CO_3 , the solution of which is hydrolysed.

Thallic chloride, $TlCl_3 \cdot 4H_2O$, is formed by passing chlorine into thallous chloride suspended in water, and evaporating at 60° .

On addition of bromine and alkali to a solution of thallous hydroxide a brown precipitate of thallic hydroxide $Tl(OH)_3$, or $TlO(OH)$, is formed which loses water on heating and forms reddish-brown thallic oxide, Tl_2O_3 . This dissolves in concentrated hydrochloric acid and forms thallic chloride $TlCl_3$ (Berry, 1922).

Thallic sulphide Tl_2S_3 , is a black pitch-like mass obtained by fusing thallium with excess of sulphur. Thallic sulphate $Tl_2(SO_4)_3 \cdot 7H_2O$ is formed by dissolving thallic oxide in dilute sulphuric acid; it is decomposed by water with precipitation of a basic salt $Tl(OH)SO_4 \cdot 2H_2O$ and forms with potassium sulphate a compound $K_2SO_4 \cdot Tl_2(SO_4)_3 \cdot 8H_2O$, which is not a true alum.

An oxide Tl_3O_5 , is said to be deposited on the anode in the electrolysis of a solution of Tl_2SO_4 faintly acidified with oxalic acid. A yellow crystalline thallium sesquichloride Tl_2Cl_3 is formed by heating thallium with nitrosyl chloride. The splendid black crystalline thallium tri-iodide TlI_3 , formed by digesting TlI with a solution of iodine in alcohol and evaporating, is a thallous poly-iodide $TlI \cdot I_2$, isomorphous with RbI_3 and CsI_3 , and not a thallic compound.

In its analogies to the alkali-metals, lead, aluminium, ferric iron, and gold, thallium shows a great diversity of properties: Dumas appropriately called it the "ornithorhynchus amongst the metals"—the duckbill platypus. Thallium is used to a limited extent in the production of a very refractive optical glass, obtained by fusing the carbonate with sand and red lead.

THE RARE EARTHS.

The substances known as the rare earths are the basic oxides of metals which all belong to the third group in the periodic table. Their general formula is M_2O_3 : the most stable cerium oxide, however, is CeO_2 , there are oxides Pr_2O_3 , Pr_4O_7 (or Pr_6O_{11}), and Tb_4O_7 , and several compounds in which rare earth metals are bivalent. They occur in rare minerals found in Scandinavia, Siberia, Greenland, the United States, and Brazil, usually in the form of silicates. Not only are some of these elements present in small amounts in the crust of the earth, but they occur mostly in a few special localities. Their compounds, until the discovery of the monazite deposits of India, Brazil and Carolina, were in the hands of a small number of chemists. The properties of many members of this group of elements are imperfectly known. In addition the elements are separated only with great difficulty.

Crookes concluded in 1887 that the rare earths might contain mixtures of closely related elements, the atomic weights of which were very near together. He called these *meta-elements* and supposed that many of the ordinary chemical elements might be of similar constitution. Improved methods of separation of the rare earths have not confirmed Crookes's hypothesis.

As an example of the difficulties encountered in this branch of chemistry, reference may be made to the separation of an earth called "didymia," regarded as a pure substance, into samaria and didymia by Lecoq de Boisbaudran (1879), and the resolution of didymia into two earths neodymia and praseodymia by Auer von Welsbach (1885). The "didymium" salts were colourless but in solution showed absorption bands in the green and red. By repeated crystallisation of the double Na and NH_4 nitrates from nitric acid two fractions were obtained, one green (praseodymium salt) and the other rose-coloured (neodymium salt), showing separately the two parts of the absorption spectrum of the original substance. The colours are complementary and the mixture, as in the case of a mixture of cobalt and nickel salts, is colourless. Since neodymia and praseodymia nearly always occur with the other earths, the absorption bands in the spectrum, even of light reflected from the sand or native earth, is an indication of the presence of rare earths.

The rare earths often show very beautiful phosphorescence effects on exposure to cathode rays in vacuum tubes, and the phosphorescence spectra were studied by Crookes. It has been found, however, that the pure earths are not phosphorescent but show the effect only in presence of small amounts of impurities.

Rare earth minerals.—Minerals containing the rare earths occur in relatively few localities and each mineral usually contains a number of the earths, and sometimes niobium and tantalum (Group V) elements, as well as titanium, zirconium, and thorium (Group IV elements). Cerite contains lanthanum, praseodymium, neodymium and samarium, in addition to cerium and traces of other earths: gadolinite contains chiefly yttrium, erbium, etc., with only small amounts of cerium and lanthanum.

Some of the best known minerals are : *cerite* $H_2(Ca, Fe)Ce_2Si_2O_{13}$, *orthite* $AlOHCa_2(Al, Fe, Ce)_2(SiO_4)_3$, *gadolinite* $(Fe, Be)_2Y_2Si_2O_{10}$, *xenotime* YPO_4 , *fergusonite* $YNbO_4$, *Australian fergusonite* $YTaO_4$, *euxenite*, *polycras*, *blomstrandite*, and *priorite*, containing also Nb, Ta, and Ti ; *saskarskite*, containing also U, Th, Nb, Ta ; and *yttrotalite*, $Y_4(Ta_2O_7)_3$. An important source of cerium and lanthanum is *monazite* (p 846).

The rare earths are usually divided into two groups :

I. **Cerite earths** : oxides of lanthanum, cerium, praseodymium, neodymium, samarium and europium. (Promethium, atomic number 61, in the group is an artificial element).

II. **Gadolinite earths** : oxides of scandium, yttrium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

Separation of rare earths.—The rare earth elements resemble one another very closely and are very difficult to separate. They are precipitated by oxalic acid in *acid* solution, and the oxides are formed by heating the oxalates. The principal methods of separation comprise :

- (1) Fractional decomposition of the nitrates by heat.
- (2) Fractional precipitation with bases.
- (3) Fractional crystallisation of salts and double salts with ammonium nitrate, bismuth nitrate, etc. (the usual method).
- (4) Fractional precipitation of salts with oxalic acid, succinic acid, potassium stearate, etc.

A fractional crystallisation is represented diagrammatically by Fig. 380. A large quantity of solution is allowed to crystallise and six (say) crops of crystals are removed in succession, represented by the top row of black dots, leaving a mother-liquor represented by a mother-liquor represented by S_1 . Each crop is now recrystallised, giving a solid and a mother-liquor represented by dots and circles on the second line.

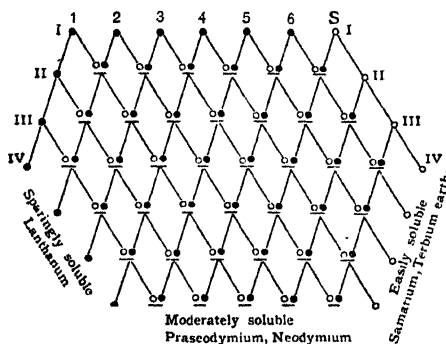


FIG. 380.—Diagram illustrating separation of rare earths.

the fractions of the third row are obtained, and so the process goes on. In the separation of ytterbium and lutecium, Urbain used 15,000 crystallisations.

(5) By ion-exchange, using a cation-absorbing resin with acidic groups (p. 185). The solution is passed down a column packed with granules of the resin, and the rare earths are removed in the top layers

A solution of ammonium citrate and citric acid is then passed down. The rare earths are selectively removed and the solution flowing from the column contains them in succession. A very complete separation can be made in this way.

The progress of the separation may be controlled by the examination of the flame, arc, spark, absorption, and X-ray spectra, and the rare earth compounds usually give pronounced and characteristic lines and bands, many being coloured. The X-ray spectra are particularly important in having settled the number and individuality of the rare earth elements.

Chemical properties of the rare earths.—The rare earths occupy a place between the strongly basic alkaline earths and weakly basic alumina, the least basic being scandium oxide and the most basic lanthanum oxide, which absorbs carbon dioxide from the air. The salts are not usually hydrolysed in solution. Some salts and oxides are coloured.

The colours of salts are :

- (a) Ce^{IV} orange, Pr green, Nd red-violet, Sm topaz-yellow, Eu pale rose.
(b) Dy bright green, Ho rose, Er deep rose, Tm bluish-green.

Salts of other rare earth elements are colourless. Traces of a coloured oxide may give an intense colour to a white oxide : 1.5 per cent of terbium oxide renders gadolinium oxide ochre-brown.

The metals are obtained by the electrolysis of the chlorides, or by heating the chlorides with alkali metals (Klemm and Bommer, 1937). They are yellowish-white, brilliant and fairly resistant in air. On heating they absorb hydrogen or nitrogen, forming hydrides (*e.g.* LaH₃) or nitrides (*e.g.* LaN). Metallic cerium mixed with lanthanum and other rare earth metals is obtained by the electrolysis of the chlorides of the metals in the residues from the extraction of thorium from monazite (p. 846). The mixture, called "mixed metal," is used in alloy with iron in automatic lighters, since when abraded it throws off showers of hot sparks which will kindle coal gas or petrol vapour.

The hydroxides are precipitated by alkali and are insoluble in excess : lanthanum hydroxide turns moist red litmus paper blue and (also the oxide) absorbs carbon dioxide from the air. The oxides, generally M₂O₃, are obtained by heating the nitrates, hydroxides or oxalates in air. They are mostly amorphous and dissolve in dilute acids even after ignition. On addition of hydrogen peroxide and alkali, peroxide hydrates (HO)₂M·O·OH are precipitated from solutions of the salts.

The anhydrous chlorides MCl₃ are obtained by heating the oxides in a stream of chlorine mixed with carbonyl chloride or sulphur chloride vapour. They are non-volatile and soluble in water, alcohol and pyridine. Lower chlorides (reducing agents) are SmCl₂, EuCl₂ and YbCl₂. The sulphides M₂S₃ (also La₂S₄ and Pr₂S₄) are hydrolysed by water and are prepared by dry methods, *e.g.* heating the anhydrous sulphates in hydrogen sulphide. The sulphates M₂(SO₄)₃ do not form alums ; those of the gadolinite earths usually crystallise with 8H₂O. The nitrates

$M(NO_3)_3$ usually crystallise with $6H_2O$ and are isomorphous with bismuth nitrate. Since the rare earths (except scandium oxide) are fairly strong bases they form normal carbonates $M_2(CO_3)_3$.

Cerium forms two series of compounds, the cerous CeX_3 and ceric CeX_4 . The cerous salts are stable and colourless, usually similar in composition to and isomorphous with the corresponding compounds of other rare earth elements. Cerium dioxide CeO_2 , the stable oxide, contains quadrivalent cerium, and cerous oxide Ce_2O_3 is obtained by reduction of the dioxide with calcium. Cerous hydroxide $Ce(OH)_3$ is formed as a white precipitate on addition of alkali to solutions of cerous salts but is rapidly oxidised by air, becoming red and violet and finally pure yellow when ceric hydroxide $Ce(OH)_4$ is produced.

Cerium dioxide is a white powder with a faint yellow tinge if traces of praseodymium are present, and the commercial oxide is usually yellowish-brown. It is used in gas mantles (p. 846). A yellow solution of ceric sulphate $Ce(SO_4)_2$, made by dissolving CeO_2 in sulphuric acid, is an oxidising agent and is used in volumetric analysis.

Atomic structure of rare earth elements.—The peculiar position of the rare earth elements in the Periodic Table and their chemical properties were explained by Bohr on the assumption that the $4f$ quantum level is empty as far as lanthanum, the electrons going into the higher levels $5s$, $5p$, $5d$ and $6s$ by preference, since some of these represent lower energies (p. 431). Only when these are partly filled does the $4f$ level begin to fill up, and as this requires 14 electrons to complete the group of 32 in all the 4-quantum levels, there will be 15 rare earth elements from lanthanum to lutecium, inclusive. Each has the same external electron configuration and hence

At. no.	Element	Numbers of electrons				Colours of M^{+++} ion	Valencies	μ^* for M^{+++}	
		4f	5s	5p	5d				6s
57	La	0	2	6	1	2	0	3	0
58	Ce	1	2	6	1	2	0	3, 4	2.56
59	Pr	2	2	6	1	2	green	3, 4	3.61
60	Nd	3	2	6	1	2	red	3, 4?	3.66
61	Pm	4	2	6	1	2	—	—	—
62	Sm	5	2	6	1	2	yellow	2, 3	1.55
63	Eu	6	2	6	1	2	red	2, 3	3.4
64	Gd	7	2	6	1	2	0	3	7.9
65	Tb	8	2	6	1	2	0	3, 4	9.7
66	Dy	9	2	6	1	2	yellow	3	10.6
67	Ho	10	2	6	1	2	orange	3	10.6
68	Er	11	2	6	1	2	red	3	9.6
69	Tm	12	2	6	1	2	green	3	7.6
70	Yb	13	2	6	1	2	0	2, 3	4.5
71	Lu	14	2	6	1	2	0	3	0
72	Hf	14	2	6	2	2	$0(M_4^+)$	4	$0(M_4^+)$

very similar chemical properties, and the atoms differ only in the nuclei and the number of electrons in the deep inner 4-quantum level. In hafnium the 5*d* level contains two electrons which, with the two electrons in the 6*s* level, make it quadrivalent, so that it belongs to Group IV.

Owing to the incomplete inner 4*f* levels from La to Yb, the rare earth compounds are (i) often coloured and (ii) paramagnetic, and they are *transitional elements* in the wider sense. The ions Sc^{+++} , Y^{+++} , La^{+++} , Ce^{++++} and Lu^{+++} are diamagnetic, since they either have no 4*f* electrons, or in the case of Lu^{+++} , a complete 4*f* group. In Ce^{+++} the single 4*f* electron has functioned as a valency electron and has been removed. The ions from Ce^{+++} to Yb^{+++} have 4*f* electrons and are paramagnetic. In the table, μ^* gives the effective paramagnetic moment of the trivalent ion. The "active" electrons in the 4*f* levels are partly screened by the completed 5*s* and 5*p* levels, and except in the case of cerium do not function as valency electrons. The so-called *lanthanide contraction* is shown by the radii in Å. of the 3-valent ions :

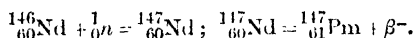
Sc 0.83 Y 1.06.

La 1.22 Ce 1.18 Pr 1.16 Nd 1.15 Sm 1.13 Eu 1.13.

Gd 1.11 Tb 1.09 Dy 1.07 Ho 1.05 Er 1.04 Tm 1.04 Yb 1.00 Lu 0.99.

With Sc and Y (non-lanthanide) there is an *expansion* of 0.23Å, whilst in passing from La to Lu (lanthanide) there is a total *contraction* of 0.23Å. The introduction of an electron into the 4*f* level, deep within the atom, produces only a negligible effect, whilst the increasing nuclear charge exerts an increasing attraction on the outer valency electrons (the same in all the elements from La to Lu) and hence gives rise to a contraction.

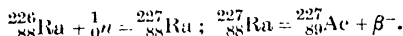
Element No. 61 is a member of the rare earth group but does not seem to occur naturally. It is formed by neutron bombardment of neodymium and has been called *promethium*, Pm :



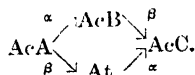
It has been obtained in milligram amounts as part of the fission product of uranium which contains the rare earths.

ACTINIUM

This is a natural radioactive element derived ultimately from the uranium isotope ${}^{238}\text{U}$ and directly by α -ray change from protoactinium (p. 402). Milligram amounts have been made artificially by neutron irradiation of radium :



Actinium undergoes a branch-change disintegration, most of it forming radioactinium by a β -ray change as shown on p. 402 but about 1 per cent undergoes α -ray change to form francium (p. 716). Actinium forms an emanation, the first product of the decay of which is actinium A. This undergoes a branch change, nearly all of it forming actinium B, but a very minute amount forms astatine, a seventh group element :



CHAPTER XLII

GROUP IV METALS

THE fourth group contains two non-metals, carbon and silicon, and seven metals.

Sub-Group <i>b</i> (Odd Series)						
	C	Si	Ge	Sn	Pb	
Atomic number - -	6	14	32	50	82	
Electron configuration	2·4	2·8·4	2·8·18·4	2·8·18·18·4	2·8·18·32·18·4	
	Diam. Graph.					
Density - - -	3·52	2·25	2·49	5·35	7·3	11·34
Atomic volume - -	3·4	5·3	11·4	13·6	16·3	18·27
Melting point - -	3500°	1420°	958·5°	231·84°	327·4°	
Boiling point - -	4200°	2600°	2700°	2260°	1620°	

Sub-Group <i>a</i> (Even Series)				
	Ti	Zr	Hf	Th
Atomic number - -	22	40	72	90
Electron configuration	2·8·10·2	2·8·18·10·2	2·8·18·32·10·2	2·8·18·32·18·10·2
Density - - -	4·50	6·53	13·07	11·3
Atomic volume - -	10·64	14·0	13·66	20·5
Melting point - -	1725°	1600°	2200°	1845°
Boiling point - -	> 3000°	> 2900°	3200°	> 3000°

Apart from tin and lead the elements have high melting points, and all have very high boiling points.

The differences between the odd and even series are ill-defined and the electrochemical characters are not very pronounced, the group forming the transition between the electropositive (base-forming) elements of Group III and the electronegative (acid-forming) elements of Group V. The group as a whole occupies the middle of the periods it comprises and hence has a somewhat neutral character, this being particularly marked in the case of carbon, which has only covalency and no electrochemical character.

The division of the Group IV elements into the two series Ge, Sn, Pb and Ti, Zr, Hf, Th is fairly obvious, but the relation of these to the "typical elements C and Si is far from clear. The increase of electropositive character from Ge to Pb and from Ti to Th, as shown *e.g.* by the capacity for sulphide formation, is clear, and the heats of formation of the oxides and chlorides increase from C to Si, indicating that Si is more electropositive than C.

this respect the *b* or odd series differs from those of earlier groups, in which the electropositive character decreases with increase in atomic weight. Mendeléeff grouped C and Si with Ge, Sn, Pb (as here), whilst Lothar Meyer grouped them with Ti, Zr and Th, with which (*e.g.* in their high m. pts., formation of covalent compounds and their predominating quadri-valency) they show close analogies.

All Group IV elements show some amphoteric character, corresponding with their position between the positive elements of Groups I and II and the negative elements of Groups V-VII, and this is probably related to their capacity for forming complex acids, which begins with Si (Abegg, 1909). In the group Ti to Th, Th alone forms definite oxy-salts and is the most electropositive element of the whole group.

The elements C, Si, Ge, Sn and (possibly) Pb all form *gaseous hydrides* RH_4 (C and Si also form others, in which the element is always 4-valent), the stability decreasing with increase of atomic weight, so that PbH_4 has only a doubtful existence. The other elements all absorb hydrogen and may form solid hydrides.

The elements all form volatile covalent *tetrachlorides* RCl_4 , which except CCl_4 are hydrolysed by liquid water. Tin and lead form lower chlorides $SnCl_2$ and $PbCl_2$ which are very stable.

C, Si and Ge all form *chloroforms* $RHCl_3$. The b.pts. of the halogen compounds in the two sub-groups are :

CCl_4	76.7°	$CHCl_3$	61.2°	$TiCl_4$	136.4°
$SiCl_4$	56.8°	$SiHCl_3$	31.8°	$ZrCl_4$	sublimes
$GeCl_4$	86.5°	$GeHCl_3$	75.2°	$HfCl_4$	„
$SnCl_4$	114.1°	—	—	$ThCl_4$	m.pt. 820°, sublimes
$PbCl_4$	decomposes	—	—		

Silicon is somewhat anomalous. *Oxychlorides* $ROCl_2$ are formed by C, Si, Ge, Zr and Th.

The typical *oxide* is RO_2 , stable in the case of all the elements, and on the whole weakly acidic (true peroxides, usually hydrated, are formed only in sub-group *a*). Lower oxides are also known, and in the case of Sn and Pb the bivalent compounds are generally most stable, the only stable compounds of 4-valent Pb being PbO_2 and some complex compounds. The oxides SnO and PbO are distinctly basic though amphoteric. All the dioxides except CO_2 have high m.pts., but this really depends on the lattice structure (p. 659); only CO_2 forms a molecular lattice of high volatility, whereas silicon shows a great reluctance to form double bonds and SiO_2 is a crystalline solid in which each Si is linked by *single* bonds to *four* oxygens. The high m. pts. of the elements C, Si, Ge, Ti, Zr, Hf and Th are also a result of lattice structure, as they (and also grey tin) form diamond lattices. Bivalent lead shows close

analogies with barium, *e.g.* PbSO_4 is very sparingly soluble and is isomorphous with BaSO_4 , with which it often occurs.

Titanium shows valencies of 2, 3 and 4 and is a member of a transitional series : Ti, V, Cr, Mn and Fe (p. 431).

TIN

History.—It is supposed that some Egyptian hieroglyphics and the word *bedil* in the Old Testament refer to tin, and tin articles occur at least as early as the Eighteenth Dynasty (c. 1400 B.C.) in Egypt. The metal is mentioned by Homer as *kassiteros*, and Pliny speaks of *plumbum nigrum* (lead) and *plumbum candidum* (tin), observing that the latter was brought from the Islands of Cassiterides in the Atlantic. This refers to the British Isles, and the island Iktis on the coast of Britain which (according to Diodorus Siculus) was separated from the mainland only at high water, is St. Michael's Mount, Cornwall. The metal was afterwards called *stannum*.

Occurrence.—Traces of native tin have been reported in Siberia, Guiana, Bolivia, and New South Wales, but the only important source is the ore *tinstone* or *cassiterite*, the crystalline dioxide SnO_2 , which is found in Cornwall, the islands of Banca and Singkep (Dutch East Indies), the Malay Peninsula and Burma, Nigeria and South Africa, and Bolivia. It occurs either massive in lodes or veins or as an alluvial deposit (*stream tin*). It is a dense mineral, easily separated from lighter rocks by washing the crushed ore. If *wolfram* (ferrous tungstate, FeWO_4) occurs with the tinstone it cannot be separated in this way, since its density is the same as that of tinstone : it is removed by roasting and electromagnetic separation (p. 6), or by heating with soda-ash, when soluble sodium tungstate is formed.

Metallurgy.—The ore after separation from gangue, wolfram, etc., may be smelted. "Tin concentrate" which contains iron pyrites, arsenical pyrites or copper sulphide is first roasted in an inclined revolving tube-furnace (Oxland and Hocking's calciner). The sulphur and arsenic are expelled as sulphur dioxide and arsenic trioxide (As_2O_3), the latter being condensed in chambers. Copper and iron form oxides and sulphates. The calcined ore discharged from the lower end of the furnace is cooled and soaked in water to remove copper sulphate which goes into solution (from which copper is recovered), and ferric oxide and light matter which are washed away. The treated ore, known as *black tin*, is mixed with ground anthracite coal and some lime or fluorspar to form a slag, and smelted in a reverberatory or a shaft furnace ("Cornish tin-castle") : $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}$. The slags contain much tin and must be worked up by smelting in a blast furnace with coke.

The tin is refined by *liquation*, *i.e.* by heating bars of the metal on the hearth of a reverberatory furnace, when the readily fusible tin flows

away, leaving a dross consisting of an alloy of tin with copper, iron, and arsenic. The metal is then fused and "poled" with billets of green wood, when the remaining impurities separate as a scum and the pure metal is obtained. Good commercial tin is 99.90 – 99.97 per cent pure. The scum and dross are worked up by smelting.

Properties.—Metallic tin has a bright white colour and a low melting point. When heated to 200° it becomes brittle and can be broken by a hammer into pieces called *grain-tin*. On slowly cooling molten tin, crystals are formed. The metal is not very ductile and is too soft to be drawn, but it is very malleable and can be rolled into *foil*, when the crystalline structure is destroyed. A bar of tin emits a creaking noise ("cry") when bent, perhaps due to a mechanical twinning of the crystals. (Zinc and cadmium behave similarly). Since tin is not easily oxidised at the ordinary temperature, tin-foil is used for wrapping chocolate, etc., and tin tubes for containing tooth-paste. The lustre of tin is not impaired by exposure to air or water, separately or conjointly, whereas lead is attacked. Tin readily alloys with iron and copper. Tinplate is made by dipping clean sheets of iron (given a bright surface by "pickling" in dilute sulphuric acid) into molten tin covered with melted palm oil. The sheet then passes under a partition into molten tin covered with melted fat, and then through rollers to remove superfluous metal.

Tin is recovered from scrap tinplate by the *detinning process*. The material is washed with alkali to remove grease, rinsed and dried, and treated with chlorine gas in iron cylinders, kept cool. Volatile stannic chloride SnCl_4 is formed and the residue of iron scrap is hydraulically pressed into blocks and smelted.

When ordinary tin is strongly cooled it crumbles to a grey powder of smaller density (5.8). The change is quickest at -50° . **Grey tin** is an enantiotropic form (p. 451) the transition point is 13.2° . White tin is metastable at a lower temperature and in cold climates, e.g. in Russia, tin sometimes falls to powder. (Aristotle seems to have known this.)

Tin is precipitated from a solution of a stannous salt by zinc, iron or aluminium; a piece of zinc suspended in the solution deposits a bright crystalline "tree" and large crystals are formed by adding a suspension of zinc dust to stannous chloride solution.

Tin oxidises when fused in air: the grey scum or dross forming on the surface is a mixture of tin dioxide and unchanged tin and on heating in air it is converted into tin dioxide SnO_2 , which is yellow when hot but becomes white on cooling. At a white heat tin burns in air with a white flame. At a very high temperature it decomposes steam: $\text{Sn} + 2\text{H}_2\text{O} = \text{SnO}_2 + 2\text{H}_2$. Tin combines with chlorine and with sulphur.

Tin is only slowly attacked by dilute hydrochloric acid, but readily dissolves in hot concentrated hydrochloric acid forming a solution of **stannous chloride**: $\text{Sn} + 2\text{HCl} = \text{SnCl}_2 + \text{H}_2$. Dilute sulphuric acid does not dissolve pure tin, but hot concentrated sulphuric acid gives **stannous sulphate** and sulphur dioxide, and some sulphur also separates, as with zinc: $\text{Sn} + 2\text{H}_2\text{SO}_4 = \text{SnSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$.

Dilute nitric acid slowly dissolves tin forming **stannous nitrate** and ammonium nitrate:



Aqua regia easily dissolves tin, forming stannic chloride; phosphoric acid dissolves tin to form **stannous phosphate** SnHPO_4 . Pure tin is not attacked by boiling concentrated sodium hydroxide solution.

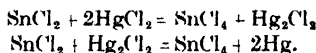
Concentrated nitric acid free from water has no action on tin, but in presence of a trace of water it acts violently, producing red fumes and forming a small quantity of soluble tin salt with an abundant white residue of hydrated stannic oxide, sometimes called metastannic acid $\text{H}_2\text{Sn}_5\text{O}_{11}$ (?). Boyle (1675) remarked that "*aqua fortis* eats up more tin than it dissolves."

Tin forms important alloys, e.g. *bronze* (p. 722). A mixture of 1 part of lead and 2 parts of tin is ordinary *fine-solder* (*soft-solder* consists of equal parts of tin and lead, cheap solder is 7 lead and 3 tin). *Old pewter* contains 4 parts of tin and 1 part of lead, usually with a little antimony. *Britannia metal* and *modern pewter* consist of tin, antimony and copper. Mirrors are sheets of very clean glass backed by pressing them on a surface of amalgamated tin-foil, but they are now mostly silvered. *Phosphor tin* is a white metallic coarsely crystalline mass formed by adding phosphorus to molten tin.

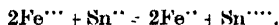
TIN COMPOUNDS

Tin forms two series of compounds: the **stannous compounds** SnX_2 in which tin is bivalent, and the **stannic compounds** SnX_4 in which tin is quadrivalent. The stannous compounds readily oxidise to stannic compounds, and stannous compounds are reducing agents.

A solution of stannous chloride added to a solution of mercuric chloride gives first a white precipitate of calomel and if added in excess a grey precipitate of metallic mercury:



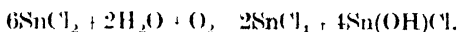
Stannous chloride added to a solution of ferric chloride and potassium ferricyanide gives a precipitate of Prussian blue, owing to the reduction of the ferric salt to a ferrous salt:



Stannous oxide SnO is more basic than tin dioxide SnO_2 , but both show feeble acidic properties forming **stannites** and **stannates**, e.g. Na_2SnO_3 and Na_2SnO_4 , which are largely hydrolysed in solution. Stannous oxide is

weaker base than lead monoxide PbO , and does not form a carbonate. Stannous salts ionise to form the stannous ion Sn^{++} , but stannic compounds (which are mostly covalent) usually form complex ions, and the existence of the stannic ion Sn^{+++} is doubtful.

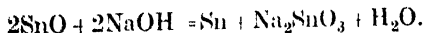
Stannous compounds.—Tin (*e.g.* foil or granulated) readily dissolves in hot concentrated hydrochloric acid to form a solution of **stannous chloride**: $Sn + 2HCl = SnCl_2 + H_2$. On evaporating and cooling, the solution deposits transparent readily fusible crystals of $SnCl_2 \cdot 2H_2O$. They lose some acid on heating and anhydrous stannous chloride is best prepared as a transparent glass by passing hydrogen chloride over heated tin. It is soluble in alcohol or ether, melts at 246° and boils at 603° , the vapour being associated: $Sn_2Cl_4 = 2SnCl_2$. The fused chloride is an electrolyte. The crystals of hydrated chloride, known as *tin salt*, do not give a clear solution except in a small amount of water or unless hydrochloric acid is added; with much water white **stannous oxychloride** $2Sn(OH)Cl \cdot H_2O$ is precipitated. Unless granulated tin is added the acid solution quickly becomes turbid from oxidation, stannous oxychloride being deposited and stannic chloride remaining in solution:



With concentrated hydrochloric acid stannous chloride forms crystalline **hydrochlorostannous acid** $HSnCl_3 \cdot 3H_2O$, and in solution H_2SnCl_4 . These give stable crystalline salts, the **chlorostannites**, *e.g.* $(NH_4)_2SnCl_4$. Stannous chloride forms several compounds with ammonia.

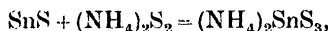
Stannous bromide $SnBr_2$, m. pt. 215.5 , is light yellow and is prepared in a similar way to stannous chloride. **Stannous iodide** SnI_2 , m. pt. 316° , is red; $SnI_2 \cdot 2H_2O$ crystallises from a solution of stannous chloride and potassium iodide; it is sparingly soluble in water but dissolves in hydriodic acid to form $HSnI_3$, salts of which are known.

Sodium hydroxide solution added to a solution of stannous chloride gives a white precipitate of **hydrated stannous oxide**, $3SnO \cdot 2H_2O$. On heating this loses water and forms **stannous oxide** SnO , a black crystalline powder. Stannous oxide is also formed by heating stannous oxalate: $SnC_2O_4 = SnO + CO + CO_2$. It smoulders when heated in air, forming tin dioxide SnO_2 . The precipitate of hydrated stannous oxide is soluble in acids forming stannous salts, and in alkali forming **stannites**, *e.g.* Na_2SnO_2 . The stannite solution has strong reducing properties; it is unstable and deposits black SnO on standing. Very concentrated alkali decomposes hydrated stannous oxide into spongy tin and a solution of sodium stannate:

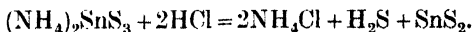


Stannous sulphide SnS is formed as a brown precipitate when hydrogen sulphide is passed into acidified stannous chloride solution, or as a

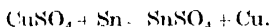
grey crystalline mass on heating tin with sulphur. The brown precipitate (black when dry) is soluble in hot concentrated hydrochloric acid (arsenic trisulphide is insoluble); it is insoluble in alkali sulphides if these are free from excess of sulphur, but dissolves readily in the polysulphides, e.g. yellow ammonium sulphide, forming **thiostannates** :



from which acids precipitate **stannic sulphide** :



Stannous sulphate SnSO_4 is best prepared by boiling tin with copper sulphate solution acidified with sulphuric acid, filtering from copper, evaporating and crystallising :



Stannic compounds.—Tin resembles carbon and silicon in forming a gaseous tin hydride SnH_4 .

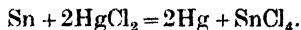
This is obtained, mixed with hydrogen, by the action of hydrochloric acid on an alloy of tin and magnesium. The pure compound is prepared by electrolysis a solution of tin sulphate containing 0.5 per cent of dextrin between platinum electrodes, washing the hydrogen (containing 0.01 per cent of SnH_4) with water and alkaline lead acetate solution, drying by passing through tubes cooled at -80° to -100° , and condensing in liquid air; the solid melts at -150° . The liquid is then fractionated at low temperatures. The gas is stable in a glass vessel for some days at room temperature, but is rapidly decomposed in presence of minute traces of tin and in contact with CaCl_2 and P_2O_5 . It decomposes rapidly and completely above 150° , does not react with dilute alkali, dilute hydrochloric acid, dilute or concentrated nitric acid, copper sulphate or lead acetate, but is absorbed by concentrated sulphuric acid or concentrated alkali, solid alkali, soda lime and silver nitrate solution (giving a black precipitate containing tin and silver).

Stannic halides are :

	SnF_4 .	SnCl_4 .	SnBr_4 .	SnI_4 .
M. pt. - - -	Sublimes	-33°	30°	143.5°
B. pt. - - -	705	114.1°	293°	340°
Density - - -	4.78	$2.234(15^\circ)$	$3.340(35^\circ)$	4.696

Solutions of halogen compounds of quadrivalent tin contain the un-ionised substances and hydrolysis products, e.g. colloidal stannic oxide; the solution in hydrochloric acid contains the ion SnCl_6^{--} , and it is doubtful if the stannic ion Sn^{++++} is ever present.

Tin combines at room temperature with chlorine gas to form a colourless volatile strongly fuming liquid **stannic chloride**, discovered by Libavius in 1605 and called *spiritus fumans Libavii*. He obtained it by distilling tin with mercuric chloride :



It is conveniently prepared by passing dry chlorine to the bottom of a

cooled vertical tube containing granulated tin until the metal is mostly converted to liquid stannic chloride, which is then distilled (b. pt. 114.1°). The vapour density corresponds with the formula SnCl_4 . With a small quantity of water it dissolves with evolution of heat, forming a clear solution from which crystalline hydrates are obtained. The hydrate $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ is prepared in commerce and called "oxymuriate of tin" or "butter of tin". Stannic chloride is obtained in detinning scrap tinplate (p. 827). The hydrate is used as a mordant, especially for silk, and in "weighting" silk. By acting on $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ with hydrogen chloride gas and cooling at 0° , crystals of hydrochlorostannic acid $\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$ are formed. Direct combination of stannic chloride with alkali chlorides gives chlorostannates, e.g. $(\text{NH}_4)_2\text{SnCl}_6$, which crystallises anhydrous and was formerly used as a mordant in dyeing madder-reds and pinks (hence it was called "pink salt"); it has been superseded for this purpose by $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Stannic chloride combines with many substances such as PCl_5 , POCl_3 , and NH_3 .

Stannic bromide SnBr_4 , a white fuming crystalline solid, and **stannic iodide** SnI_4 , yellow stable octahedral crystals, are formed directly. The **fluoride** SnF_4 , from SnCl_4 and anhydrous HF , forms white deliquescent crystals. It forms complex salts, e.g. K_2SnF_6 , analogous to fluosilicates.

Stannic oxide SnO_2 is formed by heating tin in air and by heating the product of the action of concentrated nitric acid on tin. It is a soft white powder, called *putty powder* and used for polishing and for making opaque milk-glass and white glazes. It has acidic properties, forming **stannates** with alkalis:



They are hydrolysed by water and react alkaline.

Sodium stannate $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, used as a mordant, is prepared by fusing tin dioxide with sodium hydroxide, extracting with hot water and crystallising. The ignited dioxide (or the mineral tin-stone) is insoluble in all acids except concentrated sulphuric, and does not dissolve in aqueous alkalis. It can be brought into solution only by fusion with caustic alkalis or alkali sulphides (forming thiostannates). Orthostannates are rare: the green cobalt salt Co_2SnO_4 is obtained by heating the oxides with a flux. Potassium and sodium stannates $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ have been formulated as $\text{K}_2[\text{Sn}(\text{OH})_6]$ and $\text{Na}_2[\text{Sn}(\text{OH})_6]$, analogous to K_2SnCl_6 , since the water cannot be removed without decomposition and $\text{K}_2[\text{Sn}(\text{OH})_6]$ is isomorphous with $\text{K}_2[\text{Pt}(\text{OH})_6]$.

Colloidal stannic acid, formed in solutions of stannic chloride in water, readily gelatinises. The precipitate is soluble in excess of potassium or sodium hydroxide, forming a stannate. Acids precipitate from this a

hydrochloric acid is identical with a solution of stannic chloride in water. On standing this solution slowly deposits β -stannic acid.

By the action of fairly concentrated nitric acid on tin the final product is a white curly powder of hydrated stannic oxide, which differs from α -stannic acid in being insoluble in dilute acids. It is slightly soluble in water and the solution reddens litmus. This variety of hydrated stannic oxide is called β -stannic acid or metastannic acid.

It was given the formula $H_2Sn_5O_{11}$ but the proportion of water is variable and the difference between the α - and β -acids seems to be due to something more than varying hydration. They have been regarded as colloids with particles of different sizes. Metastannic acid adsorbs phosphoric acid almost quantitatively from solutions and may be used in the separation of this acid in qualitative analysis, although it is not altogether satisfactory.

Both α - and β -stannic acids are soluble in alkali hydroxide and carbonate solutions and are reprecipitated by acids with their original properties. Boiling concentrated sulphuric acid dissolves β -stannic acid and when the cooled solution is poured into water α -stannic acid is precipitated. On fusing β -stannic acid with alkali an α -stannate is formed.

α -stannic acid when dried at 100° has the composition H_2SnO_3 ; β -stannic acid when dried in vacuum was found by Fremy (1848) to contain 11.3 per cent of water, and from this and the composition of the salts he adopted the formula $(H_2SnO_3)_5$, i.e. $H_2Sn_5O_{11} \cdot 4H_2O$, and called it metastannic acid. Cold solutions of alkalis form sparingly soluble metastannates e.g. $Na_2Sn_5O_{11} \cdot 4H_2O$, a crystalline powder, from which acids reprecipitate β -stannic acid.

Engel (1897) by the action of concentrated hydrochloric acid on β -stannic acid obtained a gelatinous mass, partly soluble in water. The filtrate gives with hydrochloric acid a white precipitate which on drying in vacuum forms a glass of the composition $Sn_5O_9(Cl_2 \cdot 4H_2O)$, soluble in dilute hydrochloric acid, but reprecipitated by the concentrated acid. It is called β -stannyl chloride or metastannyl chloride. On boiling or adding sulphuric acid to the solution β -stannic acid $Sn_5O_9(OH)_2 \cdot 4H_2O$ is quickly precipitated. The white powder obtained by the action of concentrated nitric acid on tin may be the corresponding nitrate, $Sn_5O_9(NO_3)_2 \cdot 4H_2O$.

If β -stannic acid is heated with water at 100° , it passes according to Engel into parastannic acid, $H_2Sn_5O_{11} \cdot 2H_2O$, which with hydrochloric acid forms a chloride $Sn_5O_9Cl_2 \cdot 2H_2O$. Kleinschmidt (1918) was unable to prepare parastannic acid. Engel's results may be summarised as follows:

Acid	Dried in air	Dried at 100°	K salt	Chloride
Orthostannic	H_2SnO_4	H_2SnO_4	K_2SnO_3	$SnCl_4$
Metastannic	$H_2Sn_5O_{11} \cdot 9H_2O$	$H_2Sn_5O_{11} \cdot 4H_2O$	$K_2Sn_5O_{11} \cdot 4H_2O$	$Sn_5O_9Cl_2 \cdot 4H_2O$
Parastannic	$H_2Sn_5O_{11} \cdot 7H_2O$	$H_2Sn_5O_{11} \cdot 2H_2O$	$K_2Sn_5O_{11} \cdot 2H_2O$	$Sn_5O_9Cl_2 \cdot 2H_2O$

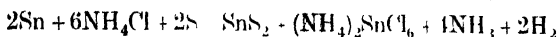
Mecklenburg (1909-14), who prepared specimens of β -stannic acid by heating a dilute solution of stannic sulphate or precipitating it with potassium sulphate, found the water content variable, and concluded that the supposed α - and β -stannic acids are colloidal hydrated stannic oxide with particles of different sizes, those of β -stannic acid being larger. The

X-ray patterns of both are identical with that of natural cassiterite or SnO_2 .

The different chemical properties are difficult to explain on this basis. Thessen and Korner (1931) found six breaks in the dehydration curves of hydrated stannic oxide corresponding with $\frac{1}{2}$, 2, $\frac{7}{4}$, $\frac{3}{2}$, 1 and $\frac{1}{2}$ H_2O for 1 molecule of SnO_2 .

Perstannic acid corresponds with the unknown *parovald* SnO_3 . By grinding stannic hydroxide with 30 per cent H_2O at 70° and drying the residue, $\text{H}_2\text{SnO}_4 \cdot 2\text{H}_2\text{O}$ is obtained, if dried at 100° $\text{H}_2\text{SnO}_4 \cdot 3\text{H}_2\text{O}$ is formed. By treating a stannate in the same way perstannates (e.g. $\text{K}_2\text{SnO}_6 \cdot 2\text{H}_2\text{O}$) are formed (Tanatar, 1905).

Stannic sulphide SnS_2 is formed by precipitating a solution of a stannic salt with hydrogen sulphide. The precipitate is light yellow but becomes black on drying, it is a mixture of tin dioxide and tin sulphide. Crystalline SnS_2 is obtained as a residue of golden yellow glistening scales called *mosaic gold* by heating a mixture of tin amalgam or filings, sulphur and sal ammoniac, as described in a fourteenth century Naples MS.



It is insoluble in acids but dissolves in *aqua regia* or alkalis.

Sodium orthothioannate $\text{Na}_2\text{SnS}_4 \cdot 18\text{H}_2\text{O}$ is formed by heating sodium stannate solution with sodium sulphide. From a solution of it boiled with precipitated SnS_2 , the metathioannate $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$ crystallises at room temperature. The metathioannate is also formed by boiling tin and sulphur with a solution of sodium sulphide.

The atomic weight of tin is found from the analysis of SnCl_4 and SnBr_4 , the valency is found from the vapour densities of SnCl_4 and tin triethyl $\text{Sn}_2(\text{C}_2\text{H}_5)_6$, and the atomic heat of tin.

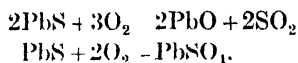
LEAD

History.—The metal lead is easily reduced from its ores and was known in ancient Babylonia and Egypt, it occurs in early bronzes and a small lead statue in the British Museum is attributed to the First Dynasty (3400 B.C.) in Egypt. Lead is mentioned in Job xix, it was apparently at first confused with tin, but it has a separate name ($\mu\delta\lambda\beta\beta\sigma\varsigma$) in Homer and the difference was recognised by Pliny (p. 826). The Greeks obtained lead from the Laurion mines but made little use of it. The Romans obtained lead from Spain, Gaul and Britain, and used it largely for cisterns, water pipes, etc. There is a considerable amount of Roman lead at Bath.

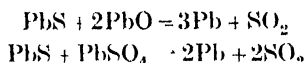
Occurrence.—Lead is widely distributed. traces occur in the native form but the chief ore is *galena*, the sulphide PbS , which is heavy (density 7.5), has a bright lustre and is found in many parts of the United Kingdom, Broken Hill (New South Wales), Spain and North America. Galena usually contains 0.01 to 0.1 per cent of silver. The oxides *lead ochre* PbO and *plattnerite* PbO_2 are rare, the carbonate

cerussite PbCO_3 , chlorophosphate *pyromorphite* $3\text{Pb}_3(\text{PO}_4)_2$, PbCl_2 , sulphate *anglesite* PbSO_4 , sulphocarbonate *leadhillite* $3\text{PbCO}_3 \cdot \text{PbSO}_4$, and basic sulphate *lanarkite* $\text{PbSO}_4 \cdot \text{PbO}$, all occur less abundantly than galena.

Metallurgy.—Lead is produced from galena by simple roasting in an oxidising atmosphere: its extraction was carried on in England during the Roman occupation. The process is mostly carried out in a reverberatory furnace (Fig. 719) known as a Flintshire furnace, or on the Scotch hearth (which has come into use again in a modified form), a flat hearth with *tuyeres* for the blast. The ore is first roasted at a moderate temperature when some galena is oxidised to lead oxide and sulphate



The temperature is then raised, a little quicklime is added and the smelting reaction takes place, the remaining lead sulphide reacting with the two oxidised products:



The slag, which contains some lead, is afterwards worked up by heating with lime and powdered coal in a small blast furnace.

Poorer ores and an increasing amount of richer ores containing quartz, zinc blende, and pyrites, are now smelted in small blast furnaces with coke. The ore is first roasted and the lead oxide is reduced in the blast furnace by the coke and carbon monoxide, the lead sulphide by the iron formed by reduction of the iron oxide in the charge (or added to the charge): $\text{PbS} + \text{Fe} = \text{FeS} + \text{Pb}$. Lead fume (chiefly PbO) formed during smelting is collected in flues and bag-filters, or by electrostatic precipitation.

Lead is also extracted by wet processes. The ore is roasted to sulphate, the soluble sulphates of manganese, magnesium, etc., dissolved out, and the lead sulphate dissolved in saturated brine containing chlorine. The solution is then electrolysed to deposit spongy lead.

The crude lead contains copper, antimony and bismuth, which make it hard. It is *softened* by melting on the hearth of a reverberatory furnace, until the foreign metals are oxidised and form a scum on the surface, mixed with a little litharge (PbO). It is then *desilvered* (p. 734). In the *Harris process* the foreign metals are removed by treating the lead with molten sodium hydroxide and nitrate. Lead is refined by electrolysis in a solution of lead fluosilicate (PbSiF_6) with a little gelatin, when a coherent deposit is formed. Commercial lead of 99.99 per cent purity is easily obtained.

Properties.—Lead if pure has a silver-white lustre, but it is usually bluish-grey. It is very soft, dense (density 11.35) and fusible. It boils at a high temperature in a nearly perfect vacuum and the vapour is

monatomic at 1870°. Lead is plastic, especially when heated, when it may be "squirted" into wire by forcing it through a die under pressure, or "wiped" in forming pipe-joints in plumbing. Tubing is also formed by squirting. "Compo" tubing is of lead hardened with a little antimony. Bearing-metal alloys contain lead with calcium, barium, lithium, sodium, etc. Crystals of lead are obtained by precipitating it from a solution of the nitrate by a suspended piece of zinc ("lead tree"). Very beautiful crystals are obtained if the solution is gelatinised by adding gelatin.

Lead oxidises rapidly but superficially in moist air to a white film of hydroxide and carbonate. *Pyrophoric lead* (obtained by heating the tartrate in a tube and then sealing) ignites spontaneously in air and burns to PbO. The metal is not attacked by pure water (except at the boiling point) or by dry air, but is rapidly corroded by soft water containing dissolved air and carbon dioxide, forming a loose deposit of hydroxide which is appreciably soluble in water and makes it poisonous. The "plumbosolvency" is prevented by calcium bicarbonate or sulphate in hard water (p. 187). Addition of a trace of tellurium reduces the corrosibility of lead and gives the metal greater strength.

Lead readily dissolves in dilute nitric acid or hot concentrated sulphuric acid forming salts of the bivalent Pb^{++} ion, which is colourless and resembles the barium ion Ba^{++} . It is a powerful cumulative poison, *i.e.* small quantities below the poisonous dose accumulate in the system and ultimately induce chronic poisoning. A characteristic symptom of lead poisoning, to which painters, plumbers and potters using lead and its compounds are liable, is a blue line on the edges of the gums.

Lead forms two series of compounds, the plumbous compounds (sometimes called "plumbic") in which it is 2-valent, and the plumbic compounds in which it is 4-valent.

The so-called "plumbous" compounds, *e.g.* Pb_2O said to be formed on heating lead oxalate, are mixtures of bivalent lead compounds and finely-divided metallic lead: $2Pb(C_2O_4) \cdot Pb + PbO + CO + 3CO_2$.

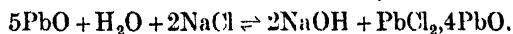
PLUMBOUS COMPOUNDS

Lead dichloride, plumbous chloride, or simply "lead chloride" $PbCl_2$, occurs as the mineral *cotunnite* in some volcanic craters. *Mendipite* $PbCl_2 \cdot 2PbO$ and *matlockite* $PbClF$ occur native. The chloride is slowly formed on heating the metal in chlorine. Boiling concentrated hydrochloric acid slowly dissolves lead: $Pb + 2HCl = PbCl_2 + H_2$. Lead chloride is usually prepared as a white precipitate by adding a chloride to a solution of a lead salt: $Pb^{++} + 2Cl^- = PbCl_2$.

It is sparingly soluble in cold water (0.91 per cent) but more soluble in boiling water (3.2 per cent) and on cooling the hot solution anhydrous

needles separate. Lead chloride melts at 498° and boils at 956° ; the vapour density at 1070° corresponding with PbCl_2 . It dissolves in concentrated hydrochloric acid and crystalline salts, e.g. $\text{NH}_4\text{Pb}_2\text{Cl}_6$, are known.

On boiling litharge (PbO) with a solution of common salt partial decomposition occurs with formation of sodium hydroxide (Scheele, 1773)



On heating the solid product yellow lead oxychloride $\text{PbCl}_2 \cdot 4\text{PbO}$ or *Turner's yellow*, used as a pigment, is formed. *Cassel yellow* $\text{PbCl}_2 \cdot 7\text{PbO}$ prepared by heating litharge with ammonium chloride, is probably a mixture.

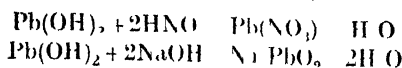
Lead chlorate $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, formed from litharge and chloric acid evolves oxygen and chlorine on heating. **Lead fluoride** PbF_2 and **lead bromide** PbBr_2 are formed by precipitation.

Lead iodide PbI_2 is formed as a yellow powder by adding potassium iodide solution to a solution of lead nitrate or acetate. It is sparingly soluble in cold water (0.06 per cent at 15°), but on boiling it dissolves (4.34 gm. per lit.) and on cooling golden-yellow spangles separate. It is soluble in a large excess of potassium iodide, forming K_2PbI_4 , but deposits again on dilution.

Lead monoxide PbO is formed on heating lead in air. The grey dross produced is a mixture of lead monoxide and metallic lead and if heated in an iron vessel it turns yellow, forming the monoxide as a yellow powder (which darkens on heating) called *massicot*; if fused a reddish-yellow scaly crystalline mass of *litharge* is obtained. Lead monoxide is reduced by heating with carbon monoxide, hydrogen or carbon. Litharge obtained in the refining of silver is largely used in making flint-glass, glazing pottery, preparing lead salts, and making paints and varnishes. It accelerates the absorption of oxygen by linseed oil, causing the oil to "dry" or form a solid oxidised compound. If litharge is boiled with water and olive-oil, **lead oleate**, a sticky adhesive mass used in making lead-plaster, is formed and glycerol passes into solution. There are two crystalline forms of PbO , a rhombic (yellow) and a tetragonal (red), which are formed by heating lead hydroxide with 10N and 15N potassium hydroxide solution, respectively. The transition temperature is 585° .

Lead hydroxide $2\text{PbO} \cdot \text{H}_2\text{O}$ or $\text{Pb}_2\text{O}(\text{OH})_2$ is formed as a white gelatinous precipitate on adding an alkali hydroxide to a lead salt solution. It may be obtained crystalline. It loses water on heating at 145° , forming the monoxide. Lead hydroxide is slightly soluble in water (as is PbO , which first forms the hydroxide) and the solution turns litmus blue. It dissolves both in acids and alkalis (except ammonium

forming lead salts and plumbites respectively and hence it is amphoteric



The plumbite, e.g. Na_2PbO_2 , is largely hydrolysed in solution



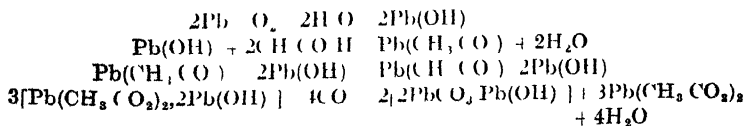
Ammonia does not dissolve lead hydroxide since a sufficient concentration of hydroxide ion cannot be produced

An important salt is lead acetate $\text{Pb(CH}_3\text{COO)}_2 \cdot 3\text{H}_2\text{O}$ called *sugar of lead* on account of its sweet taste (it is poisonous). It is prepared by dissolving lead oxide (PbO) or basic carbonate in hot dilute acetic acid, evaporation and crystallisation. Excess of lead oxide forms a sparingly soluble basic salt. By boiling litharge with a solution of lead acetate a solution of a basic acetate called *Goulard's extract* is formed, which is used as a lotion.

Solutions of lead salts give with a solution of alkali carbonate in the cold a heavy white crystalline precipitate of lead carbonate PbCO_3 . The precipitate is sparingly soluble in water (0.05 mg per lit.) but dissolves readily in a solution of ammonium acetate. The basic carbonate $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ is the white pigment called *white lead*.

Good white lead is *opaque*—it mixes readily with linseed oil and has a good covering power. If imperfectly made it is crystalline and has a considerable degree of transparency, its covering power being reduced. White lead is readily blackened by hydrogen sulphide in the atmosphere. Its adulteration by the cheaper barium sulphate is detected by the insolubility of the latter in dilute nitric acid. *Lead white* is a mixture of equal parts of white lead and barium sulphate. In *Dutch white* the proportions are one to three.

The so-called *Dutch process* (fully described by Theophrastus in 300 B.C.) produces the best quality of white lead. Rolls of sheet lead or grids of cast lead are placed in earthenware pots with vinegar. The pots are loosely covered and stacked in rows covered with planks and interstratified with spent tan-bark, the fermentation of which keeps the pots warm and produces carbon dioxide. Basic lead acetate is probably first produced and is then decomposed by the carbon dioxide, the lead acetate set free again entering into reaction



The plates after four or five weeks are encrusted with white lead. This is stripped off and ground and washed with water. The moist paste is dried in vacuum ovens. The presence of bismuth in the lead gives an objectionable colour to the product.

By boiling litharge with lead acetate solution a basic acetate is formed, which is precipitated by carbon dioxide. The white lead made by this method (*Thenard's process*) is of inferior quality. A better product is obtained by passing carbon dioxide into a suspension of lead oxide in water containing a little lead acetate.

Lead nitrate $\text{Pb}(\text{NO}_3)_2$, discovered by Libavius (1597), is deposited in anhydrous milky-white crystals, isomorphous with barium nitrate, from a solution of lead, litharge or lead carbonate in dilute nitric acid. Excess of lead oxide must not be used, as a basic salt is then formed. Clear crystals deposit from dilute nitric acid. Lead nitrate is very soluble in water (56.5 gm. in 100 gm. water at 20°).

Concentrated nitric acid precipitates lead nitrate from solution, and lead is not dissolved by concentrated nitric acid because a protective coating of nitrate is formed. On heating, lead nitrate evolves nitrogen dioxide and oxygen (with decrepitation): $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$. The reaction is reversible in a sealed tube at 357°. A basic nitrate $\text{Pb}(\text{OH})\text{NO}_3$ is formed in crystals by boiling a solution of the nitrate with litharge, and cooling.

Lead orthophosphate $\text{Pb}_3(\text{PO}_4)_2$ and **pyrophosphate** $\text{Pb}_2\text{P}_2\text{O}_7$ form white precipitates on adding the sodium salts to a solution of lead nitrate or acetate. The orthophosphate dissolves in boiling phosphoric acid and crystals of PbHPO_4 separate. $\text{Pb}(\text{H}_2\text{PO}_4)_2$ is formed by dissolving $\text{Pb}_3(\text{PO}_4)_2$ in 90 per cent phosphoric acid, evaporating and washing the crystals with ether.

Lead burns in sulphur vapour forming a greyish-black mass of lead sulphide PbS , which occurs as *galena*. The sulphide is formed as a black precipitate on passing hydrogen sulphide into a lead salt solution. It dissolves in boiling dilute nitric acid with separation of sulphur; concentrated nitric acid converts it completely into the insoluble sulphate PbSO_4 ; it dissolves in hot concentrated hydrochloric acid: $\text{PbS} + 2\text{HCl} = \text{PbCl}_2 + \text{H}_2\text{S}$.

H_2S passed into a solution of a lead salt containing excess of hydrochloric acid first forms a yellow or red precipitate of $\text{PbS}, \text{PbCl}_2$. This afterwards forms black PbS (*cf.* HgS , p. 794). On diluting a solution of PbS in concentrated hydrochloric acid, $\text{PbS}, 4\text{PbCl}_2$ is precipitated.

Plumbous persulphide PbHS_2 is formed as a dark reddish-brown solid by the action of sulphur on a solution of *s*-butyl lead mercaptan in benzene. With hydrochloric acid it forms H_2S_2 (Duncan and Ott, 1931).

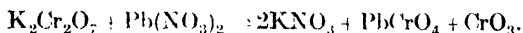
Lead sulphate PbSO_4 occurs in the mineral *anglesite* in crystals isomorphous with barytes (BaSO_4) and celestine (SrSO_4) but sometimes as pseudomorphs of galena, from which it has been formed by oxidation. It is precipitated by sulphuric acid or a sulphate from a lead salt solution.

tion as a heavy white powder, sparingly soluble in water (0.04 gm./lit. at 15°) and almost insoluble in dilute sulphuric acid (0.004 gm./lit. in 0.5 per cent acid at 15°). It dissolves in warm ammonium acetate solution (BaSO_4 is insoluble) forming feebly ionised lead acetate or a complex ion $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)'$. It also dissolves (6 per cent) in hot concentrated sulphuric acid and deposits in crystals on cooling; the compounds $\text{M}_2\text{Pb}(\text{SO}_4)_2$, where $\text{M} = \text{Na}, \text{K}$ and NH_4 , are known. With ammonia the basic sulphate $\text{PbSO}_4 \cdot \text{PbO}$ is formed.

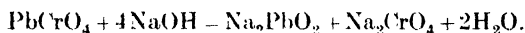
"Sublimed white lead," a mixture of 75PbSO_4 , 20PbO and 5ZnO , is formed by burning galena containing zinc in an oxidising atmosphere and collecting the fumes.

Lead chromate PbCrO_4 is formed as a yellow precipitate insoluble in dilute but soluble in concentrated nitric acid (*cf.* BaCrO_4), and used as a pigment (*chrome yellow*). It is the least soluble lead salt and is precipitated in presence of ammonium acetate.

When a lead salt is added to a solution of potassium dichromate an equilibrium is set up unless an acetate is added :



The acetate removes the chromic acid. PbCrO_4 dissolves to a yellow liquid in concentrated sodium hydroxide solution and a chromate and plumbite are formed :



Lead cannot be separated completely from acid radicals in the ordinary process used in qualitative analysis, boiling with sodium carbonate, if a chromate is present. If the solution is reduced with H_2S , a chromic salt and a precipitate of PbSO_4 are formed.

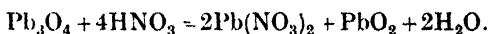
Orange or red basic lead chromates are formed when lead chromate is boiled with dilute alkali hydroxide and are used as pigments. Mixtures of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments. In calico-printing the cloth is mordanted with a lead salt and then steeped in potassium chromate solution.

PLUMBIIC COMPOUNDS

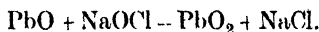
When white lead, massicot or finely-ground litharge is heated in air at about 340° it absorbs oxygen and forms a scarlet crystalline powder of *red lead* or *minium* : $6\text{PbO} + \text{O}_2 \rightleftharpoons 2\text{Pb}_3\text{O}_4$. Above 450° this decomposes again into lead monoxide and oxygen. Red lead is used to make cements with oil (it is not suitable for a pigment, as it oxidises the oil too rapidly) and in the manufacture of flint glass.

When red lead is stirred with concentrated nitric acid it is decomposed into lead monoxide which forms lead nitrate, and lead dioxide PbO_2 which remains as a chocolate-brown or puce-coloured powder on

washing out the lead nitrate with hot water and drying. It may also be prepared by boiling red lead with diluted nitric acid, filtering and washing :

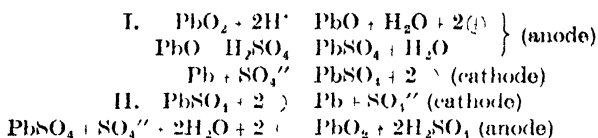


It is precipitated by bleaching powder or sodium hypochlorite solution from a solution of a plumbite :



None of these preparations is pure lead dioxide, which is difficult to obtain ; the best method is to electrolyse a solution of lead nitrate when it is deposited on the anode.

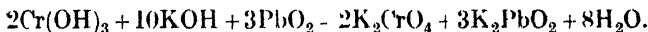
Lead dioxide is used as the anode in the lead accumulator, the cathode being metallic lead and the electrolyte dilute sulphuric acid ; in the action of the cell both electrodes tend to be converted into lead sulphate, the reaction being reversed on charging the cell :



Lead dioxide is a powerful oxidising agent. A mixture with sulphur ignites on trituration, burning with a brilliant flame and forming lead sulphide. Lead dioxide becomes red-hot when warmed in sulphur dioxide and lead sulphate is formed : $\text{PbO}_2 + \text{SO}_2 = \text{PbSO}_4$. If a manganoous salt (*e.g.* MnSO_4) is boiled with nitric acid and lead dioxide a pink solution of permauganic acid is formed (*Crum's test*) :



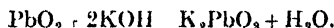
Chromic hydroxide in presence of alkali is oxidised to a chromate :



Lead dioxide is a rather weak acidic oxide forming **plumbates**.

When litharge and quicklime are heated in air the mass takes up oxygen to form calcium orthoplumbate : $4\text{CaO} + 2\text{PbO} + \text{O}_2 = 2\text{Ca}_2\text{PbO}_4$. On heating more strongly this decomposes, evolving oxygen, and the method was once used in preparing oxygen from the atmosphere.

Potassium or sodium metaplumbate is formed when lead dioxide is added to potassium or sodium hydroxide fused in a silver dish :



The plumbates crystallise as $\text{K}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$, and have been formulated as $\text{K}_2[\text{Pb}(\text{OH})_6]$ and $\text{Na}_2[\text{Pb}(\text{OH})_6]$, but the sodium can be dehydrated at 110° without decomposition and seems to contain water of crystallisation. They are hydrolysed by water, PbO_2 be

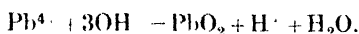
precipitated. Orthoplumbic acid H_4PbO_4 is not known, but **metaplumbic acid** H_2PbO_3 or $O=Pb(OH)_2$ is deposited as a black powder on the anode by electrolysing a slightly alkaline solution of sodium lead tartrate.

Minium, or red lead, may be regarded as plumbous orthoplumbate Pb_2PbO_4 .

Lead sesquioxide Pb_2O_3 is a yellow powder precipitated by sodium hypochlorite from a cold solution of litharge in sodium hydroxide: $2PbO + NaOCl = Pb_2O_3 + NaCl$, or by mixing solutions of potassium plumbite and **plumbate**. It is decomposed by dilute nitric acid into lead nitrate and lead dioxide and may be regarded as plumbous metaplumbate $PbPbO_3$. Lead dioxide heated in air at 350° forms Pb_2O_3 and at 440° Pb_3O_4 .

If lead dioxide is dissolved in *cold* concentrated hydrochloric acid and chlorine passed in, a dark-brown solution containing **hydrochloroplumbic acid** H_2PbCl_6 is formed. On addition of ammonium chloride this gives a yellow precipitate of ammonium **chloroplumbate** $(NH_4)_2PbCl_6$. When this is added to cold concentrated sulphuric acid the free acid H_2PbCl_6 breaks up at once and yellow liquid lead tetrachloride or **plumbic chloride** $PbCl_4$ is deposited. This readily decomposes (sometimes explosively) on warming, with evolution of chlorine: $PbCl_4 = PbCl_2 + Cl_2$. Lead dioxide dissolves in *hot* concentrated hydrochloric acid with evolution of chlorine and formation of $PbCl_2$.

On the addition of a *little* water, $PbCl_4$ forms a crystalline hydrate but it is readily hydrolysed to a brown precipitate of hydrated lead dioxide. The ion Pb^{4+} (like Sn^{4+}) is very unstable; the insoluble dioxide is usually formed when the ion might be expected:



Lead tetrafluoride PbF_4 is formed by dissolving red lead or freshly prepared lead dioxide in 96 per cent hydrofluoric acid. It forms complex salts, Na_2PbF_6 and Rb_2PbF_6 ; K_3HPbF_8 is formed by fusing lead dioxide with KHF_2 and crystallising from concentrated hydrofluoric acid.

By electrolysis of sulphuric acid, density 1.7-1.8, below 30° with a lead anode in a porous pot, **plumbic sulphate** $Pb(SO_4)_2$ is formed in yellow crystals decomposed by water: $PbSO_4 + SO_3 = Pb(SO_4)_2$; $Pb(SO_4)_2 + 2H_2O = PbO_3 + 2H_2SO_4$. It is probably formed in the over-charged lead accumulator.

Lead tetra-acetate $Pb(C_2H_3O_2)_4$ separates on cooling in colourless needles from a solution of red lead in hot glacial acetic acid (lead dioxide is insoluble). It is decomposed by water, lead dioxide being formed, but it is the most stable plumbic salt.

A gaseous **lead hydride** has been described but its existence is very doubtful.

The **atomic weight** of lead has been found from the ratios $PbCl_2 : 2AgCl$ and $PbBr_2 : 2AgBr$. The valency is determined from the atomic heat and the vapour density of lead tetraethyl $Pb(C_2H_5)_4$. The atomic weight of lead is of special interest as it varies somewhat with the source from which the lead is derived when it has been formed in the radioactive decay of uranium ($Pb = 206$) or thorium ($Pb = 208$); ordinary lead has the atomic weight 207.2 and is a mixture of isotopes.

GERMANIUM

Germanium was discovered by Winkler in 1886 in a Freiberg mineral *argyrodite* $\text{GeS}_2 \cdot 4\text{Ag}_2\text{S}$ (5 to 7 per cent Ge). It is found in small amounts in euxenite, some zinc ores, and the ash of some coals. One method of extraction depends on the distillation of the volatile GeCl_4 with hydrochloric acid, any gallium in the solution being extracted with ether, but a better process is to extract both gallium and germanium with sodium hydroxide solution: it can be purified by electro-deposition (Sehba and Pugh, 1937). The oxide GeO_2 is reduced at a red heat by carbon or hydrogen, and the metal is precipitated by zinc from solutions of its compounds. It is greyish-white, brittle, forms octahedral crystals, and is insoluble in hydrochloric acid but soluble in nitric acid or aqua regia. It does not oxidise in air, but burns when heated in oxygen, chlorine or bromine vapour.

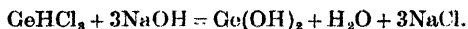
Germanium, like tin and lead, forms two series of compounds, the **germanous compounds** GeX_2 and the better known **germanic compounds** GeX_4 .

The **germanium hydrides** GeH_4 , Ge_2H_6 , and Ge_3H_8 resemble silicon hydrides and are prepared by the action of dilute hydrochloric acid on magnesium germanide Mg_2Ge (made by heating magnesium and germanium in hydrogen) condensation from the mixture with hydrogen, and fractional distillation (see p. 666). **Monogermane** GeH_4 is a gas also prepared by the action of a solution of ammonium bromide in liquid ammonia on Mg_2Ge : $\text{Mg}_2\text{Ge} + 4\text{NH}_4\text{Br} = 2\text{MgBr}_2 + \text{GeH}_4 + 4\text{NH}_3$, and is evolved with hydrogen by the action of dilute sulphuric acid and a germanium compound on zinc (Voegelé, 1902).

Germanic oxide GeO_2 is white and crystallises in two forms, isomorphous with quartz and cassiterite (SnO_2). It is non-volatile, sparingly soluble in water but soluble in hydrochloric acid forming GeCl_4 , and in alkali forming a **germanate**, e.g. Na_2GeO_3 . The hydroxide is not known and alkalis do not precipitate germanic salts.

Germanic fluoride GeF_4 is a colourless fuming gas prepared similarly to SiF_4 and forming H_2GeF_6 with water. **Germanic chloride** GeCl_4 is a colourless fuming liquid, b.pt. 86° , formed by heating germanium in chlorine, or the metal or GeS_2 with mercuric chloride. It is hydrolysed by water but distils from concentrated hydrochloric acid. **Germanium chloroform** GeHCl_3 is a colourless fuming liquid, formed (with some GeCl_2) by passing HCl gas over heated germanium. **Germanic sulphide** GeS_2 is formed as a white precipitate with H_2S in presence of excess of HCl : it is readily soluble in alkali and ammonium sulphides, forming **thiogermanates**, from which it is reprecipitated by a large excess of acid.

Germanous hydroxide Ge(OH)_2 is formed as a yellowish-red precipitate by the action of alkali on germanium chloroform:



On heating it forms grey **germanous oxide** GeO . The hydroxide dissolves in alkali to form a **germanite**, e.g. Na_2GeO_2 . Reddish-brown **germanous sulphide** GeS is formed by heating GeS_2 in hydrogen: on further heating it forms **germanium**.

The similarity of germanous and germanic compounds to stannous and stannic compounds is evident. Unlike tin, however, germanium forms only

covalent compounds; there are some stannous salts and salts of bivalent lead are common.

TITANIUM

Titanium was discovered by Gregor in 1789 in a black sand in Cornwall, now called *ilmenite* or *titaniferous iron ore*, also found in Nova Scotia and New Zealand: it is ferrous titanate FeTiO_3 . The dioxide TiO_2 occurs in three forms (cf. SiO_2): *rutile*, tetragonal prisms isomorphous with cassiterite SnO_2 , density 4.21; *anatase*, slender tetragonal pyramids, density 3.88; and *brookite*, flat rhombic prisms, density 4.17. TiO_2 is very widely distributed in iron ores, silicate rocks, clay, bauxite, coal and soil, and most commercial iron contains titanium. Titanium also occurs in small amounts in plant and animal tissues and bones.

Ferrotitanium, made in the electric furnace, is used to remove oxygen and nitrogen from molten steel, and steel containing some titanium has toughness and resistance to wear, e.g. as rails. Hydrated titanium dioxide mixed with barium sulphate is used as a pigment (*titanium white*), titanium dioxide is used in tinting artificial teeth and in making a yellow glaze for porcelain, and a solution of the trichloride TiCl_3 in dyeing as a mordant and in removing dyes from fabrics.

Titanium dioxide is manufactured from ilmenite by three processes: (i) The *acid process* (used in Norway) in which the powder is heated with concentrated sulphuric acid, the iron and titanium sulphates dissolved in water, and TiO_2 precipitated from the solution by hydrolysis. (ii) The *alkaline process* (used in the U.S.A.) in which the mineral is fused with sodium sulphide and the mass extracted with water; FeS and TiO_2 remain and the FeS is dissolved in a solution of sulphurous acid. (iii) The *chlorine process*, in which a mixture of ilmenite and carbon is heated in a stream of chlorine at 350° to chlorinate the iron and then at 550° , when volatile TiCl_4 distils and is then hydrolysed by water to TiO_2 .

Metallic titanium was first obtained impure as a black powder by Berzelius in 1825 by heating potassium fluorotitanate K_2TiF_6 with sodium. A purer metal (containing 2 per cent of carbon) was made by Moissan (1895) by reducing excess of TiO_2 with carbon in the electric furnace and remelting the metal with TiO_2 . Pure titanium is difficult to obtain as it readily combines with oxygen, nitrogen, carbon and silicon: most of the early specimens contained carbon and nitrogen, e.g. the copper-coloured cubes found in some blast furnaces are a mixture of the nitride TiN and graphite. The pure metal is obtained by (i) heating liquid TiCl_4 with sodium in a closed iron bomb, when so much heat is evolved that the titanium (m. pt. 1800°) is partly fused (Nilson and Pettersson, 1887); (ii) heating TiO_2 and calcium in a vacuum iron vessel; (iii) strongly heating a tungsten filament in TiI_4 vapour (van Arkel and de Boer, 1925). Titanium forms white very hard brittle hexagonal crystals, density 4.50; it welds at a red heat. When heated it burns in oxygen and decomposes steam; it dissolves in cold dilute sulphuric or hot concentrated hydrochloric acid with evolution of hydrogen forming *titanous salts* containing the ion Ti^{2+} , and it burns in nitrogen at 800° forming the *nitride* TiN .

Titanium forms three series of compounds in which it is 4-, 3-, and 2-valent, the important ones being the 4- and 3-valent. Some compounds contain the *titanyl radical* $=\text{Ti}=\text{O}$.

Titanium dioxide can be prepared from rutile (Wöhler, 1849) by fusing with K_2CO_3 , dissolving in dilute HF and crystallising $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ (glittering leaflets); from a solution of this in hot water ammonia precipitates white hydrated TiO_2 (*titanic acid*), on heating which TiO_2 is formed as a white powder, yellow when hot. Titanium dioxide dissolves in hot concentrated sulphuric acid to form **titanyl sulphate**, which forms crystals, $\text{TiO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$. A solution is used as a test for H_2O_2 (p. 196), the yellow or orange colour being due to **per-titanic acid**, which is formed as a bright yellow precipitate on adding H_2O_2 and ammonia to a solution of TiCl_4 in alcohol. The old formula is $\text{TiO}_3 \cdot 3\text{H}_2\text{O}$, but it is probably $(\text{HO})_3-\text{Ti}-\text{O}-\text{OH}$. Titanium dioxide also shows weakly acidic properties, forming *titanates*, e.g. $\text{K}_2\text{TiO}_3 \cdot 4\text{H}_2\text{O}$. These are derived from supposed *titanic acids*, e.g. *meta-titanic acid* H_2TiO_3 , precipitated on boiling a solution of titanyl sulphate and acetic acid for some hours (Zr is not precipitated), but the products all show only the X-ray spectrum of TiO_2 as rutile or anatase.

Titanium tetrachloride TiCl_4 , b.pt. 136.4°, is a colourless strongly fuming liquid (used along with ammonia for smoke-screens) prepared by passing chlorine over heated titanium or a mixture of TiO_2 and carbon, or chlorine or CCl_4 vapour at a high temperature over TiO_2 : $2\text{Cl}_2 + \text{TiO}_2 \rightarrow \text{TiCl}_4 + \text{O}_2$. It is soluble in water but is hydrolysed by excess, depositing hydrated TiO_2 ; with NH_4Cl and hydrochloric acid it forms yellow crystals of the compound $(\text{NH}_4)_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$.

Brown **titanic nitride** Ti_3N_4 is formed by the action of liquid ammonia and KNH_2 on TiBr_4 (Ruff and Treidel, 1912): it is decomposed by heat into TiN and nitrogen and by water into TiO_2 and ammonia. **Titanium disulphide** TiS_2 is formed in yellow scales (like SnS_2) by passing TiCl_4 vapour and H_2S through a heated tube.

The most important compound of 3-valent titanium is the **titanium trichloride** TiCl_3 , formed in dark violet scales on passing a mixture of TiCl_4 vapour and hydrogen through a heated tube (Ebelmen, 1847). On heating in hydrogen chloride it forms TiCl_3 : $2\text{TiCl}_3 + 2\text{HCl} \rightarrow 2\text{TiCl}_4 + \text{H}_2$. The solution (which is deep violet when pure but inky black if TiCl_4 is present) is formed by reducing a solution of TiCl_4 in hydrochloric acid with zinc. It is a powerful reducing agent (e.g. reducing perchlorate to chloride). Two forms of the solid hydrate $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$, violet and green, are known (cf. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$). Alkalis precipitate from TiCl_3 solution the dark-brown or blue hydrated sesquioxide Ti_2O_3 or $\text{Ti}(\text{OH})_3$; anhydrous Ti_2O_3 (a black powder or red crystals) is formed by heating TiO_2 strongly in dry hydrogen. The bronze-yellow **titanous nitride** TiN is formed from the elements or by heating TiO_2 in ammonia gas at 1400°–1500° (Ruff, 1909). It contains 3 valent titanium $\text{Ti}-\text{N}$, as is shown by dissolving in dilute H_2SO_4 and HF and titrating with KMnO_4 .

Stable violet rubidium and caesium **titanium alums** $\text{MTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ are formed by electrolytic reduction of a solution of TiO_2 and alkali sulphate in sulphuric acid.

Bivalent titanium occurs in the black **titanium dichloride** TiCl_2 , formed by heating TiCl_3 in vacuum at 400°: $2\text{TiCl}_3 = \text{TiCl}_2 + \text{TiCl}_4$, or in hydrogen

bright redness in entire absence of oxygen and moisture (Friodol and Guérin, 1875): it smoulders on heating in air forming $TiCl_4$ and TiO_2 , evolves hydrogen with water and form a green solution in concentrated hydrochloric acid. Titanium monoxide TiO is formed by heating TiO_2 in hydrogen at 2000° at 150 atm pressure.

ZIRCONIUM

Klaproth in 1789 discovered zirconium dioxide in *zircon* $ZrSiO_4$, gem forms of which are the *hyacinth* and *jargon*. *Zircon* occurs in alluvial sands in Ceylon, the Urals, Australia and North Carolina. *Baddeleyite*, found in Ceylon and Brazil, is the oxide ZrO_2 and is the chief source. *Zirkote*, a mixture of oxide and silicate, is found at Minas Geraes, Brazil. Metallic zirconium was first prepared by Berzelius in 1824 by heating K_2ZrF_6 with potassium or sodium $K_2ZrF_6 + 4K \rightarrow Zr + 6KF$.

Zircon is fused with sodium hydroxide and the mass boiled with water, when sodium silicate dissolves and impure zirconium dioxide remains. *Baddeleyite* is boiled with concentrated hydrochloric acid to remove impurities and then boiled with concentrated sulphuric acid, when *zirconyl sulphate* $ZrOSO_4$ (a compound of the *zirconyl radical* $Zr-O$) is formed. A solution of this is precipitated with ammonia and the hydrated precipitate heated to form zirconium dioxide. Zirconium dioxide mixed with rare earths is used to make Neust filaments, which conduct electrolytically when hot. Zirconium dioxide (*zirconia*) has a very high m.p. (2700°) and is used for refractory and white enamels. The precipitated hydrated zirconium dioxide is soluble in acids but insoluble in alkalis, but ZrO_2 on fusion with alkalis forms *zirconates*, e.g. Na_2ZrO_3 .

Metallic zirconium is deposited in a very pure state on a tungsten filament electrically heated in the vapour of zirconium iodide $ZrI_4 \rightarrow Zr + 2I_2$. When pure it is soft, but it usually forms hard white scales of high m.p. It forms a tough, bullet proof alloy steel. It is only slowly attacked by acids, except hydrofluoric acid and aqua regia. On heating in hydrogen it forms black *zirconium hydride*.

Zirconium is predominantly quadrivalent, but $ZrCl_3$ and $ZrCl_2$ are known. Hydrogen peroxide precipitates zirconium quantitatively as $(HO)_2Zr-O-OH$. Zirconium tetrachloride $ZrCl_4$ is a white solid, subliming at 300° , formed by passing dry chlorine over a strongly heated mixture of ZrO_2 and carbon. It is hydrolysed by water and white needles of *zirconium oxychloride* $ZrOCl \cdot 2H_2O$ are formed on evaporating a solution in hydrochloric acid. On heating $ZrCl_4$ and aluminium in hydrogen at 300° brown *zirconium trichloride* $ZrCl_3$ is formed and on heating this in vacuum at 350° it gives black *zirconium dichloride* $2ZrCl_2 \rightarrow ZrCl_2 + ZrCl_4$. *Zirconium tetrafluoride* ZrF_4 is a white solid formed by the action of anhydrous hydrofluoric acid on the tetrachloride $ZrCl_4 + 4HF \rightarrow ZrF_4 + 4HCl$. It forms *fluorozirconates* K_2ZrF_6 and K_3ZrF_7 (containing the ion ZrF_6^{--}).

Zirconium forms an indefinite basic carbonate, perhaps containing $ZrOCOC_3$.

Zirconium nitrate $Zr(NO_3)_4 \cdot 5H_2O$ may be a zirconyl compound $(ZrO)H_2(NO_3)_2 \cdot 4H_2O$, and there is a basic nitrate $ZrO(NO_3)_2 \cdot 2H_2O$; the commercial salt is indefinitely basic.

Sodium phosphate precipitates *zirconium phosphate* $ZrH_2(PO_4)_2$, insoluble in HCl but soluble in HF (serving to separate Zr from all elements except

Hf) : on heating it forms ZrP_2O_7 . Zirconium disulphide ZrS_2 , stable to water, is formed by heating $ZrCl_4$ with H_2S or sulphur vapour. Zirconium sulphate $Zr(SO_4)_2$ is formed by dissolving ZrO_2 in hot concentrated sulphuric acid, evaporating and heating the residue. It crystallises from water as $ZrO(SO_4) \cdot H_2SO_4 \cdot 3H_2O$, or $H_2[ZrO(SO_4)_2] \cdot 3H_2O$, which readily loses $3H_2O$. A neutral zirconium solution gives with potassium sulphate a precipitate of an indefinite basic double sulphate, insoluble in HCl (separation of Zr from Ti, Nb, Ta).

HAFNIUM

The element hafnium was discovered in an X-ray examination of zirconium minerals by Coster and Hevesy in 1923. It occurs in all zirconium minerals, usually 0.1 per cent or less, although baddeleyite contains 1 to 2 per cent and zircon up to 7 per cent. *Alvite* (Zr, Hf, Th) SiO_4 , and *malacone*, an altered form of zircon (with occluded argon), contain up to 60 per cent. It gives practically all the reactions of zirconium and is found in most commercial zirconium compounds (3 per cent in ordinary zirconia). It is best separated from zirconium by fractional crystallisation of the double fluorides $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$ (more soluble). The crystal of the double fluoride $(NH_4)_3HfF_7$ contains $(NH_4)_2HfF_6$ and NH_4F units (cf. Zr). The white metal (m. pt. 2200°), obtained by heating K_2HfF_6 or $HfCl_4$ with sodium, or heating a tungsten filament in HfI_4 vapour (de Boer, 1930), has been added to tungsten lamp filaments. The white dioxide HfO_2 (m. pt. 2812°) is refractory and is more basic than ZrO_2 . The white solid chloride $HfCl_4$ is more volatile than $ZrCl_4$ and sublimes at 250° . The carbide HfC and double carbide $Hf(C,4TaC)$ have probably the highest m. pts. (over 4000°) of any known substances. Other compounds are the sulphide HfS_2 and sulphate $Hf(SO_4)_2$ decomposing at a higher temperature (500°) than $Zr(SO_4)_2$.

THORIUM

Thorium was discovered in the Norwegian mineral *thorite* $ThSiO_4$ by Berzelius in 1828. *Thorianite*, found in Ceylon, is chiefly thorium oxide (70–80 per cent ThO_2) with some uranium, lead and rare earth oxides and occluded helium (9 ml. per gm.). The chief source of thorium is *monazite*, a phosphate of cerium and lanthanum with about 4–18 per cent of ThO_2 and 1 ml. of occluded helium per gm., found as sand in Brazil and at Travancore in India.

Thorium dioxide (*thoria*) ThO_2 , used for incandescent mantles mixed with 1 per cent of cerium dioxide CeO_2 (pure thoria gives a feeble light), is extracted from monazite. This is heated with concentrated sulphuric acid, thorium phosphate is precipitated and is heated with sodium carbonate to form thoria, which is then purified by a process depending on the solubility of thorium oxalate in ammonium oxalate solution, in which lanthanum and cerium oxalates are insoluble. On heating the oxalate, thorium dioxide is formed and is dissolved in nitric acid to form thorium nitrate $Th(NO_3)_4$; the commercial nitrate is approximately $Th(NO_3)_4 \cdot 4H_2O$. On heating the nitrate it decomposes, swells up, and leaves pure white thorium dioxide. Thorium dioxide is added to the tungsten filaments of some kind of electric lamps.

Metallic thorium, m. pt. 1845°, is difficult to obtain pure, as it combines with hydrogen, oxygen, nitrogen, and carbon. It may be prepared by heating a mixture of thorium tetrachloride and sodium: $\text{ThCl}_4 + 4\text{Na} = \text{Th} + 4\text{NaCl}$. It is white, soft when pure, burns brightly in air on heating, and is readily soluble in hydrochloric acid. A solid **thorium hydride** ThH_4 is formed with emission of light when thorium is heated in hydrogen.

Thorium peroxide, perhaps $(\text{HO})_2\text{Th}-\text{O}-\text{OH}$, with no acidic properties, is quantitatively precipitated by hydrogen peroxide from solutions of thorium compounds. **Thorium tetrachloride** ThCl_4 is a white solid, formed by burning the metal in chlorine, or heating a mixture of ThO_2 and carbon in chlorine, or heating ThO_2 in carbonyl chloride COCl_2 or a mixture of chlorine and the vapour of sulphur chloride S_2Cl_2 . It is not hydrolysed by water and behaves as a salt. A **basic thorium carbonate** is precipitated by alkali carbonate and is soluble in excess, but the solution becomes turbid on heating. **Thorium sulphate** $\text{Th}(\text{SO}_4)_2$ is made by dissolving thorium dioxide in concentrated sulphuric acid, evaporating, and heating to drive off the excess of acid; it forms a number of hydrates. The hydrate with $9\text{H}_2\text{O}$ increases in solubility with rise of temperature, whilst that with $4\text{H}_2\text{O}$ decreases. The common hydrate is with $8\text{H}_2\text{O}$. **Acid sulphates** $\text{H}_2[\text{Th}(\text{SO}_4)_3]$ and $\text{H}_2[\text{Th}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2]$ and many double sulphates, *e.g.* $\text{K}_2[\text{Th}(\text{SO}_4)_4], 4\text{H}_2\text{O}$, $(\text{NH}_4)_6[\text{Th}(\text{SO}_4)_5], 3\text{H}_2\text{O}$ and $(\text{NH}_4)_8[(\text{Th}(\text{SO}_4)_6], 2\text{H}_2\text{O}$ are known. There are also double nitrates, *e.g.* $(\text{NH}_4)_2\text{Th}(\text{NO}_3)_6$. The *radio-activity* of thorium is discussed on p. 401.

It should be noted that thorium alone among the elements of its subgroup (Ti, Zr, Hf, Th) forms salt-like halides, and it readily forms oxy-salts, whilst the others in their quadrivalent state mostly form covalent compounds. The compounds ThI_2 and ThI_3 , containing bivalent and trivalent thorium, are formed by heating ThI_4 with metallic thorium powder. The tetra-iodide ThI_4 is formed by heating thorium in iodine vapour.

CHAPTER XLIII

GROUP V METALS

The elements of the fifth group (apart from radioactive elements) are :

Sub-group *a* or even series : vanadium, niobium (or columbium) and tantalum.

Sub-group *b* or odd series : nitrogen, phosphorus, arsenic, antimony, and bismuth.

Sub-group <i>a</i> (Even Series)			
	V	Nb(Cb)	Ta
Atomic number	23	41	73
Electron configuration	2·8·11·2	2·8·18·12·1	2·8·18·32·11·2
Density	5·8	8·56	16·6
Atomic volume	8·8	10·85	10·9
Melting point	1710°	1950°	2850°
Boiling point	3000°	3700°	>4100°

The elements of the even series are all less common metals of high m. pt. and are **transitional elements** (p. 370).

Sub-group <i>b</i> (Odd Series)					
	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electron configuration	2·5	2·8·5	2·8·18·5	2·8·18·18·5	2·8·18·32·18·5
Density of solid	1·0265	1·83*	5·73†	6·71	9·80
Atomic volume	13·65	16·96	13·08	18·25	21·32
Melting point	- 210°	44·1°	814·5°	630·5°	271°
Boiling point	- 195·8°	287°	615°	1380°	1450°
			sublimes		

The odd series contains both non-metals and metals. Nitrogen and phosphorus, already dealt with, are definitely non-metals (although a "metallic" conducting form of phosphorus is known), antimony and bismuth definitely metals, whilst arsenic stands on the threshold between non-metals and metals and as such is sometimes called a *metalloid*. It will be considered here along with the metals. The elements all have low m. pts. and (except Sb and Bi) low b. pts. and form molecules in the vapour state composed of more than one atom : N₂, P₄, As₄, Sb₄ (?), Sb₂ (?), and Bi₂, the metals being peculiar in this respect, since most metals are monatomic. All these elements exist in allotropic forms.

The predominating valencies in the group are 3 and (except for nitro-

* White P.

† γ -arsenic.

gen) 5, although other valencies such as 4 (especially in the even series) are known. Nitrogen forms oxides, N_2O , NO , NO_2 , in which it has apparently anomalous valencies; although these are paralleled by oxides of vanadium, with nitrogen they usually result from peculiar linkages. The elements of the odd series all form compounds with metals in which they show their normal valency (*cf.* p. 676: Mg_3N_2 , Ca_3P_2 , Na_3As , Zn_3Sb_2 , Mg_3Bi_2).

The gradation of electrochemical character is well shown with the gaseous hydrides formed by all elements of the odd series. Ammonia NH_3 is a fairly strong base, forming halide and oxy-salts containing the ammonium ion NH_4 . The other hydrides (except perhaps PH_3) are not formed directly from their elements; phosphine PH_3 is very weakly basic, forming phosphonium halides PH_4X , all decomposed by water; the hydrides arsine AsH_3 and stibine SbH_3 have no basic properties; the very unstable bismuth hydride BiH_3 (?) is soluble in alkalis and may be feebly acidic. The elements of the even series do not form hydrides. Elements of the odd series all form compounds with hydrocarbon radicals, including $Bi(CH_3)_3$, etc.; these are not formed or are doubtful with elements of the even series.

The chlorides of the odd series are predominantly covalent; with nitrogen only NCl_3 is known and with arsenic and bismuth only $AsCl_3$ and $BiCl_3$, but AsF_5 and BiF_5 exist; all the other elements form RCl_3 and RCl_5 , and in the even series chlorides corresponding with other valencies. Fluorides RF_3 are known with all the elements and RF_5 with P, As and Sb.* Nitrogen chloride hydrolyses in a peculiar way, forming hypochlorous acid (p. 526), the trihalides of phosphorus are completely and irreversibly hydrolysed by excess of water into HX and the corresponding oxyacids; arsenic chloride exists in equilibrium with excess of hydrochloric acid: $2AsCl_3 + 3H_2O \rightleftharpoons As_2O_3 + 6HCl$; antimony and bismuth trichlorides are only partly and reversibly hydrolysed to basic compounds, *e.g.* $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$. The higher chlorides PCl_5 and $SbCl_5$ are dissociated by heat: $SbCl_5 \rightleftharpoons SbCl_3 + Cl_2$, etc. PCl_5 on hydrolysis forms an oxyhalide, $POCl_3$, which by further action of water loses all the halogen and forms phosphoric acid.

The stability of the halides MX_5 increases from V to Ta; only VF_5 is known, but tantalum is remarkable in forming a penta-iodide TaI_5 . Double fluorides of varying formulae are known: xKF, VO_2F , $xKF, NbOF_3$ and xKF, TaF_5 ; from solutions containing excess of HF double fluorides containing VOF_3 and NbF_5 are formed.

All the elements form many oxides, including the typical acidic pentoxides R_2O_5 . In the odd series only phosphorus, but in the even

* Iodides RI_3 and RI_5 (PI_5 is doubtful), also P_2I_4 , are known, but ordinary nitrogen iodide is $NI_3 \cdot NH_3$.

series all the elements, form pentoxides directly; the acidic character of these diminishes with increasing atomic weight. In the even series the acidity of the pentoxides decreases from V to Ta, V_2O_5 being quite strongly acidic, but the oxides Nb_2O_5 and Ta_2O_5 are more like the weakly acidic TiO_2 and ZrO_2 . Vanadium, niobium and tantalum readily combine with oxygen and their compounds are reduced with difficulty, while the oxides of the odd series elements (except phosphorus) are easily reduced. All the elements form trioxides R_2O_3 and most of them form dioxides RO_2 or R_2O_4 . In the even series these are basic, but in the odd series the trioxides are acidic with N, P, and As, amphoteric with Sb, and basic with Bi. The increase in basic properties with increasing atomic weight of the element should be noted.

All the elements except nitrogen form sulphides by direct combination. Those of nitrogen and phosphorus have peculiar formulæ and are easily hydrolysed; those of the other elements of the odd series are typical, R_2S_3 and R_2S_5 (except that bismuth forms only Bi_2S_3), while those of the even series correspond with varying valencies. Many sulphides form thio-salts such as Na_3AsS_4 with sulphides of alkali metals.

Although vanadium compounds can be reduced to the stage V^{II} in solution, niobium stops at Nb^{III} and no salts below Nb^V have been isolated from solution; Ta^V is not reduced by nascent hydrogen. Although V_2O_5 can be reduced (with difficulty) to metal by hydrogen at a high temperature, Nb_2O_5 and Ta_2O_5 are not reduced. Vanadium, niobium, and tantalum form no nitrates or carbonates, and niobium and tantalum no salts with weak acids, which are ill-defined even for vanadium.

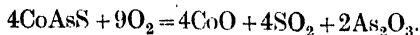
ARSENIC

History.—The red mineral *realgar* As_2S_2 and the yellow mineral *orpiment* As_2S_3 were known to the ancients. Olympiodoros (fifth century) describes *white arsenic* (arsenious oxide As_2O_3) obtained by roasting the sulphide in air, and the element itself was obtained as a sublimate and was used for whitening copper. The composition of white arsenic as the calx (oxide) of "metallic" arsenic was recognised by Brandt in 1733.

Occurrence.—Native arsenic occurs in the Harz and in Japan. Compounds which occur are the sulphides *realgar* and *orpiment*, the oxide *arsenolite* As_2O_3 , *löllingite* $FeAs_2$, *niccolite* $NiAs$, *chloanthite* $NiAs_2$, *nickel glance* $NiAsS$, *smallite* or *tin-white cobalt* $(Co, Ni, Fe)As_2$, *arsenical pyrites* or *mispickel* $FeAsS$ (isomorphous with pyrites FeS_2), and salts of arsenic acid, *pharmacolite* $CaHAsO_4 \cdot 2H_2O$, *erythrite* or *cobalt bloom* $Co_3(AsO_4)_2 \cdot 8H_2O$, and *mimetite* $3Pb_3(AsO_4)_2 \cdot PbCl_2$. Native sulphur, iron pyrites and other sulphide ores often contain arsenic, and sulphuric acid made from arsenical pyrites may contain 1 per cent of As_2O_3 . Coal smoke, especially in yellow fogs, may contain arsenious

oxide, from pyrites in the coal. Traces of arsenic occur in some mineral waters, in the soil (1-60 p.p.m.), in the adult human body (0.1 mg. per kg.), etc. American tobacco (6-30 p.p.m.) and the fresh edible parts of shell-fish (7-90 p.p.m.) contain unusually large amounts of arsenic.

In roasting minerals, e.g. *cobaltite*, in metallurgical treatment fumes of arsenious oxide may be evolved and condense in flues as a powder :



This is obtained in larger amounts by roasting arsenical ores such as *mispickel* in a current of air. Most of the arsenious oxide used is obtained from flue dust in copper, lead and tin smelting, especially in the U.S.A., Mexico and Sweden (where one smelter, on the Gulf of Bothnia, could supply the world requirement of As_2O_3). The crude oxide is sublimed in iron pots to form *white arsenic* (popularly called simply "arsenic"), the commonest arsenic compound.

Most of the arsenic is used in alloys with lead and copper ; as arsenite in weed-killer and sheep-dips, and copper, lead and calcium arsenates in sprays ; as oxide as a poison for vermin, preserving skins, in glass-making for removing colour, in enamelling, pyrotechny, wood preserving, and making pigments and mordants.

Arsenic.—The element is obtained by heating the trioxide with charcoal in a clay crucible covered with an inverted iron cone, into which the arsenic sublimes as a grey powder : $\text{As}_2\text{O}_3 + 3\text{C} = 2\text{As} + 3\text{CO}$; or by heating arsenical pyrites or *mispickel* in a clay tube fitted for half its length with an inner tube of sheet iron, into which the arsenic sublimes as a nearly white crystalline mass, which is split off by unrolling the iron tube : $\text{FeAsS} - \text{FeS} + \text{As}$. It is purified by subliming from charcoal powder. Arsenic sulphides are not reduced by heating with carbon, but are reduced when heated with potassium cyanide : $\text{As}_2\text{S}_3 + 3\text{KCN} = 2\text{As} + 3\text{KCNS}$.

Heat a little arsenious oxide in a dry test-tube with dry powdered charcoal and potassium cyanide. A black mirror of arsenic sublimes. On heating, this oxidises to a white sublimate of arsenious oxide.

Arsenic, like phosphorus, exists in allotropic forms (the designations α and γ are sometimes interchanged) :

- (1) α -arsenic or yellow arsenic, cubic, density 2.026 at 18° , soluble in carbon disulphide, and corresponding with white phosphorus ; it is very unstable and readily passes into γ -arsenic.
- (2) β -arsenic or black arsenic, amorphous, density 4.71, insoluble in carbon disulphide, corresponding with amorphous phosphorus, less stable than γ -arsenic.
- (3) γ -arsenic or grey arsenic ("metallic arsenic"), rhombohedral, density 5.73, insoluble in carbon disulphide, and corresponding with metallic phosphorus ; it is the stable and common form of arsenic.

Yellow arsenic or α -arsenic, first noticed by Bettendorff in 1867, is obtained (similarly to white phosphorus) by quickly cooling arsenic vapour. Arsenic is distilled in a current of carbon dioxide and the gas is passed into a U-tube, where it meets a current of cooled carbon dioxide, and is then passed into cold carbon disulphide, which dissolves the yellow arsenic (8 g. in 100 ml. at 20°). The solution on evaporation in the dark deposits light-yellow regular crystals, which rapidly oxidise in air at room temperature with a faint luminescence and a garlic odour. It rapidly passes into γ -arsenic when exposed to light, even at -180°. Yellow arsenic is formed quantitatively by volatilising γ -arsenic in vacuum and cooling the vapour with liquid air. Its molecular weight in carbon disulphide solution corresponds with As_4 .

Stannous chloride when heated with a solution of arsenious oxide in hydrochloric acid gives a brown precipitate of arsenic (*Bettendorff's test*), part of which is α -arsenic, soluble in carbon disulphide. The yield is increased if the mixture is shaken with carbon disulphide during the reduction, since the solution of α -arsenic is more stable than the solid.

Black arsenic or β -arsenic is formed when grey arsenic is rapidly heated in a glass tube in a current of hydrogen, when it deposits on the cooler part (200°-220°) of the tube as a shining black mirror, some grey arsenic being deposited nearer the heated part (Berzelius, 1844). It is not appreciably oxidised by air even at 80°, but at 360° it passes into γ -arsenic with strong evolution of heat.

Grey arsenic or γ -arsenic, the common variety, forms brilliant tin-white rhombohedral crystals with metallic lustre, and is a fairly good conductor of heat and electricity. It is isomorphous with metallic phosphorus (p. 568), tellurium, antimony and bismuth. It does not form an amalgam. It volatilises slowly at 100° and at 450° it sublimes rapidly without previous fusion, forming a colourless vapour, the density of which shows that it contains As_4 molecules. At higher temperatures dissociation occurs: $As_4 \rightleftharpoons 2As_2$. When heated under pressure in a sealed tube grey arsenic melts at 814°.

Grey arsenic is not oxidised in dry air at room temperature, but in moist air it rapidly becomes covered with a blackish-grey film containing arsenic trioxide, which can be removed by heating alone or with a little iodine. It begins to oxidise in air about 200° and at 250°-300° it shows phosphorescence, the temperature at which this appears in oxygen depending on the pressure, as in the case of white phosphorus. At 400° it burns in air with a white flame, which is brilliant in oxygen: $As_4 + 3O_2 = 2As_2O_3$.

Heat 1 gm. of arsenic in a current of oxygen in a hard glass tube connected with an empty flask, the exit tube passing to a U-tube packed with glass-wool to retain fumes of arsenious oxide. The arsenic burns with a white flame and white solid arsenious oxide is deposited in the flask.

Powdered arsenic takes fire in chlorine forming AsCl_3 , and inflames in contact with bromine forming AsBr_3 . It combines directly with sulphur and phosphorus on heating, but not with nitrogen or carbon. Arsenic forms fusible arsenides with most metals; 0.3-1 per cent alloyed with lead makes the metal harder and more fusible, and if this fused alloy is poured through a sieve, the drops falling down a tower into water form shot.

Hydrochloric acid dissolves arsenic only in presence of air. Dilute nitric acid has little action in the cold, but slowly oxidises arsenic to arsenious oxide when hot; concentrated nitric acid rapidly oxidises arsenic to arsenic acid H_3AsO_4 , which is rapidly formed, with some AsCl_3 , with aqua regia. Hot concentrated sulphuric acid is reduced to sulphur dioxide; unstable arsenious sulphate $\text{As}_2(\text{SO}_4)_3$ seems to be formed, but decomposes into the trioxide. Arsenic is insoluble in alkali solution but is attacked by fused alkali hydroxide, forming arsenite and hydrogen: $2\text{As} + 6\text{NaOH} = 2\text{Na}_3\text{AsO}_3 + 3\text{H}_2$; at high temperatures some arsenate is formed: $4\text{Na}_3\text{AsO}_3 = 3\text{Na}_3\text{AsO}_4 + \text{Na}_3\text{As}$.

ARSENIC HYDRIDE

Arsenic trihydride (*arsine*, or *arseniuretted hydrogen*) is not formed from the elements but is produced by the action of *nascent* hydrogen on a dilute solution of an arsenic compound (Proust, 1799). A solution of arsenious oxide is added to a mixture of zinc and dilute sulphuric acid evolving hydrogen: the hydrogen acquires a very unpleasant smell of garlic and burns with a lilac-coloured flame. Scheele discovered arsine in 1775 by the action of arsenic acid solution on zinc. It is formed at the cathode in the electrolysis of a solution of arsenious oxide, by reduction of the solution with sodium amalgam, and by warming a solution of an arsenious compound with zinc or aluminium and sodium hydroxide solution (*Fleitmann's test*, 1851; arsenates and antimony compounds do not give this reaction). *Arsenic hydride is very poisonous.*

Pure arsine is prepared by passing the mixture with hydrogen obtained by the above methods through a tube cooled in liquid air, when it condenses to a white solid, m. pt. -116.3° , b. pt. -62.4° . On warming the liquid the pure gas is evolved.

Arsine may also be prepared by the action of dilute hydrochloric acid on zinc arsenide, obtained by heating equal weights of arsenic and zinc in a closed crucible: $\text{Zn}_2\text{As}_2 + 6\text{HCl} = 2\text{AsH}_3 + 3\text{ZnCl}_2$; by the action of water on sodium arsenide, formed by passing the impure gas over heated sodium: $\text{Na}_2\text{As} + 3\text{H}_2\text{O} = \text{AsH}_3 + 3\text{NaOH}$; by heating sodium formate (dried at 210°) with sodium arsenite: $\text{Na}_2\text{AsO}_3 + 3\text{HCOONa} = 3\text{Na}_2\text{CO}_3 + \text{AsH}_3$; or (most conveniently) by the action of warm water on aluminium arsenide, obtained

by heating aluminium powder and powdered arsenic in a covered crucible : $AlAs + 3H_2O = Al(OH)_3 + AsH_3$ (the reaction may become violent.)

On exposure to light moist arsine rapidly decomposes, with deposition of black shining arsenic with a little yellow arsenic, but the pure dry gas is stable. It is decomposed by heat into its elements, the reaction beginning at about 230° : $2AsH_3 = 2As + 3H_2$. From the ratio of the volumes of arsine and hydrogen, and the density of arsine, the formula AsH_3 is found (Soubeiran, 1830). Arsine is only slightly soluble in water and ether but dissolves readily in turpentine. It does not form compounds analogous to phosphonium compounds.

The Marsh-Berzelius test.—The formation of gaseous arsine by the action of nascent hydrogen on an arsenic compound, and the ready decomposition of arsine by heat, are applied in the very sensitive Marsh-Berzelius test.

Marsh in 1836 used the deposition of arsenic on a cold surface held in the flame of the burning hydrogen containing arsine ; Berzelius (and Liebig) in 1837 passed the gas through a tube heated at one place and obtained an arsenic mirror.

Hydrogen generated from pure zinc and pure dilute sulphuric acid is freed from traces of hydrogen sulphide by a roll of dry lead acetate paper in the first part of the drying tube, the second half of which is packed with

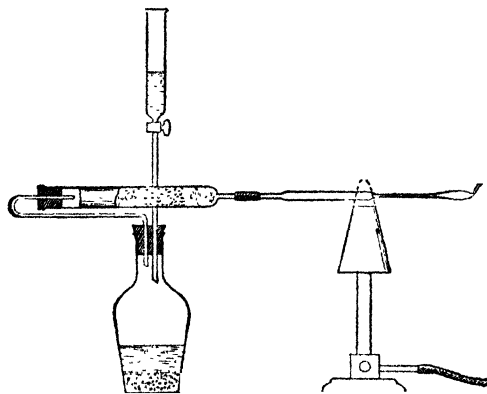


FIG. 381.— Marsh-Berzelius test for arsenic

pure granular calcium chloride, separated from the paper by a plug of cotton-wool (Fig. 381). The dry gas passes through a hard glass tube heated at one point to dull redness. If the materials are free from arsenic, no stain is produced. If a *dilute* solution of arsenious oxide or any material to be tested for arsenic is added to the flask, arsine is formed, which is decomposed in the hot tube, a brown or black mirror being deposited beyond the heated portion.

After a sufficient time, all the arsenic is evolved, and by comparing the mirror with standard tubes prepared with known amounts of arsenious oxide (0.001–0.01 mg.) a quantitative estimation may be made. A combination of Marsh's and Bettendorff's (p. 852) tests will detect 10^{-8} gm. Some varieties of zinc do not easily reduce arsenic compounds but may be activated by treatment with 2 per cent cadmium sulphate solution.

If the tube is not heated but the gas kindled at the jet, the flame is tinged lilac and deposits black spots of arsenic on the outer surface of a glazed

porcelain dish filled with water: $2AsH_3 = 2As + 3H_2$. These dissolve readily in sodium hypochlorite or bleaching powder solution, forming arsenic acid or arsenates: $2As + 5NaOCl + 3H_2O = 2H_3AsO_4 + 5NaCl$, but are insoluble in tartaric acid. If a spot is moistened with yellow ammonium sulphide, and this evaporated by gentle heating, a *bright yellow* spot of As_2S_3 is left.

The *electrolytic Marsh test* (first used by Bloxam in 1861) is now generally used. The mercury cathode, on which arsenates (not reduced at a platinum cathode) also form arsine, is contained in a porous pot, waxed except for a central part and fitted with a rubber stopper carrying a tap-funnel for introducing and withdrawing liquid and a delivery tube connected with a calcium chloride tube and the electrically heated hard glass decomposition tube. The anode is a roll of platinum foil outside the porous cell in a glass vessel. The outer vessel and porous cell contain dilute sulphuric acid. The solution to be tested is added through the tap-funnel (Fig. 382).

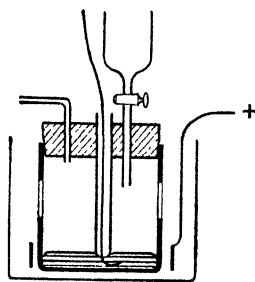
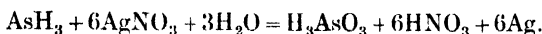
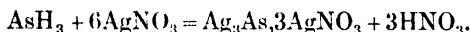


FIG. 382.—Electrolytic Marsh apparatus.

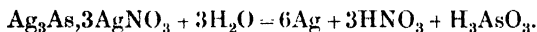
Arsine passed into *dilute* silver nitrate solution gives a black precipitate of silver and the filtrate contains arsenious acid (*cf.* antimony):



With *more concentrated* silver nitrate solution no precipitate is formed but a yellow solution of a compound of silver arsenide and nitrate:



On dilution with water, a black precipitate of silver is deposited:



Arsine with mercuric chloride gives a yellow coloration, due to the formation of $AsH(HgCl)_2$, which on further treatment gives brown $As(HgCl)_3$ and finally black As_2Hg_3 . This is the basis of the sensitive *Gutzeit test* (1879).

The solution is added to pure zinc and dilute hydrochloric acid containing a little stannous chloride (to reduce any 5-valent arsenic) in a small bottle fitted with a rubber stopper and a vertical tube containing a roll of lead acetate paper, with a bored rubber stopper at the top. A piece of filter paper previously moistened with mercuric chloride solution and dried is placed over the hole of the upper stopper and another similar stopper is placed on the top, the two being held together by a spring clip. The yellow stain on the paper is compared with standards.

A *solid arsenic hydride* As_2H_2 , is said to be formed as a brown powder by (i) the electrolysis of dilute sulphuric acid or sodium hydroxide solution with an arsenic cathode, (ii) the action of water on sodium arsenide, (iii) the action of a silent discharge on arsine, and (iv) by mixing a solution of arsenic chloride in hydrochloric acid with a solution of stannous chloride in ether. Another *brown solid hydride* As_4H_2 is said to be formed by oxidising arsine

with a solution of stannic chloride in hydrochloric acid : $4\text{AsH}_3 + 5\text{SnCl}_4 = \text{As}_4\text{H}_2 + 10\text{HCl} + 5\text{SnCl}_2$. The identity of these solid hydrides is doubtful.

By the growth of moulds in presence of arsenic compounds (e.g. Scheele's green on wall-paper) a volatile poisonous arsenic compound, trimethylarsine $\text{As}(\text{CH}_3)_3$, is formed, not arsenic hydride, as was once thought.

HALOGEN COMPOUNDS OF ARSENIC

The stable arsenic halides (including the fluoride) are covalent compounds of the type AsX_3 , the only definite halide of 5-valent arsenic being AsF_5 .

AsF_3 colourless liquid, b.pt. 60.4° , m.pt. -8.5° , dens. 2.666 at 0°

AsF_4 colourless gas, b.pt. -53° , m.pt. -80° .

AsCl_3 colourless liquid, b.pt. 130.2° , m.pt. -13° , dens. 2.205 at 0° .

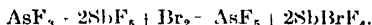
AsBr_3 colourless prismatic crystals, m.pt. 31° , b.pt. 221° , dens. 3.66 at 15° .

AsI_3 red hexagonal and rhombohedral crystals, m.pt. 140.7° , b.pt. 394.414° , density 4.39 at 15° .

As_2I_4 red prismatic crystals, m.pt. 130° , b.pt. $375^\circ-370^\circ$.

Arsenic burns in fluoro to form AsF_3 and AsF_5 . Arsenic trifluoride AsF_3 (Dumas, 1826), a colourless fuming liquid, is prepared by heating a mixture of arsenious oxide, powdered fluorspar and concentrated sulphuric acid in a lead retort : $\text{As}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AsF}_3 + 3\text{H}_2\text{O}$. It is hydrolysed by water.

Arsenic pentafluoride AsF_5 is a colourless gas obtained by distilling a mixture of arsenic trifluoride, antimony pentafluoride and bromine at a temperature not exceeding 55° , and collecting in a receiver cooled in liquid air :



Fluoarsenates $\text{K}_2\text{AsF}_7 \cdot \text{H}_2\text{O}$ and $\text{KAsOF}_4 \cdot \text{H}_2\text{O}$ are crystalline solids formed by dissolving potassium arsenate in hydrofluoric acid.

Arsenic trichloride AsCl_3 (*butter of arsenic*, Glauber, 1648), the most important halogen compound of arsenic, is formed when arsenic burns in chlorine gas (a reaction which occurs spontaneously even if the materials are very dry), or by heating arsenic with mercuric chloride, or by heating arsenious oxide in chlorine



or (usually) by distilling a mixture of arsenious oxide, sodium chloride and concentrated sulphuric acid, and condensing the vapour in a cooled receiver : $\text{As}_2\text{O}_3 + 6\text{HCl} \rightleftharpoons 2\text{AsCl}_3 + 3\text{H}_2\text{O}$. The distillate is freed from excess of chlorine by distillation over powdered arsenic. The most convenient method of preparation is to heat arsenious oxide with sulphur chloride under a reflux condenser, pass chlorine through the mixture, and distil (Partington, 1929) :



Arsenic trichloride is a colourless liquid, which in a good freezing mixture forms pearly crystals. It fumes in moist air and is hydrolysed by water: the first product is said (Wallace, 1858) to be a crystalline hydroxychloride $\text{AsCl}(\text{OH})_2$ but with excess of water arsenious oxide is formed: $2\text{AsCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{As}_2\text{O}_3 + 6\text{HCl}$. The reaction is reversible and arsenic chloride distils when arsenious oxide or an arsenite is boiled with fairly concentrated hydrochloric acid. An arsenate is not decomposed, except with fuming acid. The freezing-point diagram shows no evidence of AsCl_5 .

Arsenic tribromide AsBr_3 , a white crystalline solid, less easily hydrolysed than AsCl_3 , and arsenic tri-iodide AsI_3 , red crystals, are formed by heating arsenic with a solution of the halogen in carbon disulphide. The tri-iodide is only slightly hydrolysed by water and is precipitated on adding a solution of arsenious oxide in hot hydrochloric acid to a solution of potassium iodide. A di-iodide As_2I_4 , obtained as a dark-red mass by heating iodine with arsenic in a closed tube at 260° , is soluble in CS_2 but is decomposed by water into AsI_3 and arsenic. AsI (a brown powder formed by saturating alcoholic iodine solution with arsine) and AsI_2 (a brown solid formed by heating AsI_3 and iodine at 150°) are doubtful.

OXIDES AND OXYACIDS OF ARSENIC

Arsenious oxide (*arsenic trioxide*) is a white solid, subliming freely at about 193° . The vapour density below 800° corresponds with As_4O_6 , at 1800° with As_2O_3 . In solution in nitrobenzene the formula is As_4O_6 . Arsenious oxide exists in three forms: (i) an *amorphous glass*, dens. 3.738, m. pt. 200° , (ii) *octahedral* (the common form), dens. 3.689, m. pt. 275° , b. pt. 465° , sublims above 135° without fusion but melts under pressure, (iii) *monoclinic*, dens. 3.85, m. pt. about 312° .

The *amorphous* variety (first mentioned by Roger Bacon) is a colourless transparent glass formed when the vapour is slowly condensed at a temperature slightly below the point of vaporisation, according to Rushton and Daniels (1926) at 275° – 315° . It may be kept in a sealed tube, but at 100° or in presence of moisture it becomes opaque and very slowly passes into the octahedral form. The solubility (1 part in about 25 parts of water at 13° , or in 12 parts at 100°) decreases on standing, owing to conversion to the octahedral form.

The *octahedral* form is stable under ordinary conditions and is produced when the vapour is *rapidly* condensed, when the trioxide is crystallised from water or hydrochloric acid, or spontaneously with evolution of heat from the vitreous form. Arsenious oxide powder is not easily wetted by water and dissolves only slowly, more rapidly on boiling.

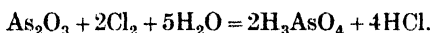
When 15 gm. of As_2O_3 are dissolved by heating in a mixture of 60 ml. of water and 90 gm. of hydrochloric acid of dens. 1.1, the crystallisation on cooling is accompanied by brilliant flashes of light (Rose, 1835).

The *monoclinic* variety, which occurs as the mineral *claudetite*, crystallises on cooling from a boiling saturated solution of the amorphous substance in alkali arsenite solution, or by sublimation under special conditions.

If arsenious oxide is heated in a sealed tube at 400° the vitreous form remains at the bottom of the tube, the monoclinic form sublimes to the intermediate part at 200°, and the octahedral to the top of the tube. The different forms may be recognised under a lens (Debray, 1864). The transition point of the octahedral and monoclinic varieties is 250° but the change is very slow (Rushton and Daniels, 1926).

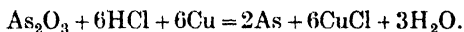
The structure of the As_2O_3 molecule is the same as that of P_4O_6 shown in Fig. 304. In the *crystal* the structure of octahedral As_4O_6 is a diamond lattice (Fig. 306) with tetrahedral As_4O_6 molecules replacing carbon atoms.

Arsenious oxide is easily *oxidised* to the pentoxide, arsenic acid or an arsenate, by ozone, hydrogen peroxide, chlorine, aqua regia, bromine, iodine, nitric acid, and hypochlorites (especially in alkaline solution):



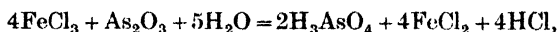
It precipitates red cuprous oxide from Fehling's solution.

Arsenious oxide is easily *reduced* to arsenic by heating with charcoal or potassium cyanide, by a solution of stannous chloride, which gives a brown precipitate: $\text{As}_2\text{O}_3 + 3\text{SnCl}_2 + 6\text{HCl} = 3\text{SnCl}_4 + 2\text{As} + 3\text{H}_2\text{O}$, and by boiling with hydrochloric acid and copper foil, which becomes grey owing to deposition of arsenic:



If the copper foil is washed, dried, and heated in a tube, a crystalline sublimate of arsenious oxide is formed (Reinsch's test, 1838). The mere change of colour of the copper is not decisive, as it is also given by selenium, mercury, antimony and bismuth compounds. Arsenates are only slowly reduced.

Arsenious oxide reduces ferric chloride solution on heating:



and arsenites in alkaline solution reduce nitric oxide to nitrous oxide.

By the action of fuming sulphuric acid and of SO_3 on the trioxide, unstable compounds of As_2O_3 with 1, 2, 3, 4, 6 and 8 SO_3 , decomposed by water, are formed: As_2O_3 then acts as a feebly basic oxide (Adie, 1889).

Small quantities of arsenious oxide occur in some mineral waters, which are used as nerve tonics, in skin diseases, and in improving the blood. It is a violent poison: 0.06 gm. is a dangerous dose and 0.125–0.25 gm. is fatal. The peasants of Styria are said to be able to consume arsenious oxide in amounts (0.3 gm.) which would ordinarily be fatal. It is said to act as a cosmetic, to improve the breathing in mountain climbing, and to give plumpness to the figure. Freshly precipitated ferric hydroxide, obtained

by adding magnesia to a solution of ferric chloride, adsorbs arsenious oxide and is recommended as an antidote.

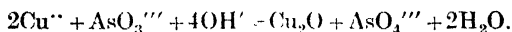
Arsenious oxide has only a feeble bactericidal action and some moulds flourish on arsenical solutions.

Arsenious acid and arsenites.—A solution of arsenious oxide in water has a feeble acid reaction and may contain arsenious acid H_3AsO_3 or $HAsO_2$, although only the trioxide crystallises on concentration or on cooling a hot solution. The acid is very weak. Arsenious oxide dissolves in solutions of alkali hydroxides or carbonates (when carbon dioxide is evolved; even warm sodium bicarbonate solution dissolves it), forming **arsenites**, which are not always well defined. They correspond with the *hypothetical* arsenious acids: *ortho* H_3AsO_3 , *pyro* $H_4As_2O_5$, and *meta* $HAsO_2$.

Although the formulae of arsenic compounds are generally analogous to those of phosphorus, arsenious acid is **tribasic** and its formula is different from that of phosphorous acid, which is **dibasic**:

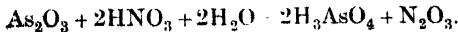


On dissolving arsenious oxide in hot sodium hydroxide solution and evaporating, a white amorphous powder of sodium arsenite Na_3AsO_3 or $NaAsO_2$ is obtained, soluble in and hydrolysed by water. A solution gives with silver nitrate a yellow precipitate of silver arsenite Ag_3AsO_3 , soluble in acetic acid (the yellow phosphate is insoluble). Copper sulphate gives a bright-green precipitate of cupric arsenite (*Scheele's green*), $CuHASO_3$ or $Cu_3(AsO_3)_2 \cdot 2H_2O$ (Bornemann, 1922), used as an insecticide and formerly as a pigment. When its solution in alkali is boiled, an arsenate is formed and cuprous oxide precipitated:



The brilliant *Schweinfurt green* or *Paris green* is a compound of cupric arsenite and acetate, with the formula $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_3)_2$, obtained by adding dilute acetic acid to precipitated copper arsenite, or by boiling basic copper acetate with acetic acid and arsenious oxide, and is used as an insecticide and an oil or water colour.

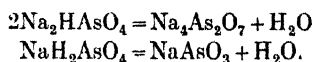
Arsenic pentoxide and arsenic acid.—Unlike phosphorus, arsenic burns in oxygen to give practically only the lower oxide As_2O_3 . Cavendish obtained arsenic acid, corresponding with arsenic pentoxide, in 1764, but did not publish the work, and the acid was independently discovered by Scheele in 1775 by oxidising arsenic trioxide with chlorine water. The acid is usually made by boiling arsenic trioxide with concentrated nitric acid:



The very concentrated solution on cooling deposits rhombic crystals of orthoarsenic acid $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ (sometimes H_3AsO_4 separates). At 100° these melt, lose water and leave a crystalline powder of $\text{H}_3\text{As}_2\text{O}_7$ or $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ (Menzies and Potter, 1912). At 160° slowly, or at 200° rapidly, the acid forms arsenic pentoxide As_2O_5 , a deliquescent amorphous solid, which dissolves slowly in water. Pyroarsenic acid $\text{H}_4\text{As}_2\text{O}_7$ is obtained in crystals by evaporating a solution of arsenic acid in an open dish until the temperature rises to 170° – 180° (Rosenheim and Antelmann, 1930). Meta-arsenic acid is not known. Arsenic pentoxide decomposes at a red heat : $\text{As}_2\text{O}_5 = \text{As}_2\text{O}_3 + \text{O}_2$.

Arsenic acid is an oxidising agent : it liberates iodine from an iodide in acid solution : $\text{AsO}_4''' + 2\text{I}^- + 2\text{H}^+ = \text{AsO}_3''' + \text{I}_2 + \text{H}_2\text{O}$, and with hot fuming hydrochloric acid it evolves chlorine (Mayrhofer, 1871) : $\text{As}_2\text{O}_5 + 10\text{HCl} = 2\text{AsCl}_3 + 2\text{Cl}_2 + 5\text{H}_2\text{O}$.

The arsenates are generally isomorphous with phosphates and have similar formulae. The normal ortho-arsenates exist both as solids and in solution, but (unlike the phosphates) the pyro- and meta-arsenates exist only as solids, prepared by heating the appropriate ortho-salts, as in the case of phosphates :



Common sodium arsenate $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ is largely used in calico-printing ; calcium, magnesium, manganese and lead (PbHAsO_4) arsenates are used as sprays for fruit trees.

Ammonium molybdate and concentrated nitric acid give with arsenates a yellow precipitate similar to that obtained with phosphates, but only on heating. Magnesia mixture gives a white crystalline precipitate of magnesium ammonium arsenate $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, similar to $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. On heating, this gives magnesium pyro-arsenate $\text{Mg}_2\text{As}_2\text{O}_7$.

Arsenates are distinguished from phosphates by giving with silver nitrate in neutral solution a light chocolate-brown precipitate of silver arsenate Ag_3AsO_4 , soluble in dilute nitric acid and in ammonia. An arsenite present may be detected by dissolving the precipitate in dilute nitric acid, avoiding excess, and adding ammonia drop by drop. Brown silver arsenate is first precipitated, then yellow silver arsenite.

ARSENIC SULPHIDES

The compounds As_3S_3 , As_2S_2 , As_2S_3 and As_2S_5 (the first somewhat doubtful) are known. The disulphide As_2S_2 occurs as the red mineral *realgar*, and the trisulphide As_2S_3 as the yellow mineral *orpiment* (= *auripigmentum*), and they are made by heating arsenic or arsenious oxide with sulphur : $2\text{As}_2\text{O}_3 + 9\text{S} = 2\text{As}_2\text{S}_3 + 3\text{SO}_2$.

The disulphide is not easily made in this way, and an impure product is made by distilling iron pyrites with arsenical pyrites: $2\text{FeAsS} + 2\text{FeS}_2 = \text{As}_2\text{S}_2 + 4\text{FeS}$.

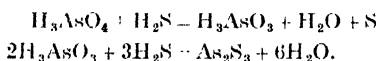
Arsenic disulphide (dens. 3.506) becomes yellow when exposed to light in air, from formation of As_2S_3 and As_2O_3 ; it becomes black at 267° owing to conversion into an allotropic form (dens. 3.254).

Arsenic trisulphide (dens. 3.43) is formed as a yellow precipitate on passing hydrogen sulphide into a solution of arsenious oxide in dilute hydrochloric acid: $2\text{AsCl}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 6\text{HCl}$. Orpiment is used as an insecticide. A mixture of the trisulphide and trioxide, made by subliming the trioxide with sulphur, was the pigment *King's yellow*, now replaced by lead chromate.

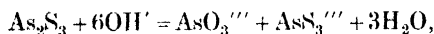
Realgar and orpiment are used in pyrotechny (*Bengal fire* is a mixture of 2 parts of realgar, 7 parts of sulphur and 24 parts of nitre), and mixed with slaked lime for removing hair; the active agent is probably calcium hydrosulphide, and sodium sulphide is now mostly used instead of the mixture.

Arsenic disulphide and trisulphide burn when heated in air, forming sulphur dioxide and volatile arsenic trioxide. They are almost insoluble in hot concentrated hydrochloric acid (antimony sulphide is readily soluble) but are oxidised by nitric acid.

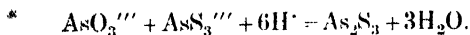
Arsenic pentasulphide As_2S_5 is formed as a light-yellow precipitate when hydrogen sulphide is passed rapidly into a warm solution of arsenic acid containing 10–12 per cent of free hydrochloric acid (Bunsen, 1878): $\text{As}_2\text{O}_5 + 5\text{H}_2\text{S} = \text{As}_2\text{S}_5 + 5\text{H}_2\text{O}$. If the reaction takes place slowly and in the cold, a white precipitate of sulphur is first formed and the arsenic acid is reduced to arsenious acid, which is then precipitated as arsenious sulphide:



Arsenic trisulphide dissolves readily in alkali hydroxide or ammonia, and even in warm ammonium carbonate solution (antimony trisulphide is insoluble). It is usually supposed that a mixture of arsenite and thioarsenite is formed:



but the thioarsenite may be hydrolysed in solution to arsenite. On acidifying, all the arsenic is precipitated as trisulphide:



When arsenic trisulphide is dissolved in an alkali sulphide, a thioarsenite alone is formed: $3\text{S}'' + \text{As}_2\text{S}_3 = 2\text{AsS}_3''$. Thioarsenites are derived from hypothetical thioarsenious acids: H_3AsS_3 (*ortho*), $\text{H}_4\text{As}_2\text{S}_5$ (*pyro*), HAsS_2 (*meta*), but (like the arsenites) have not been

much investigated. $(\text{NH}_4)_3\text{AsS}_3$ and $\text{Ca}_3(\text{AsS}_3)_2$ form colourless crystals, K_3AsS_3 and Na_3AsS_3 amorphous white powders.

When arsenic trisulphide is boiled with sodium carbonate solution, carbon dioxide is evolved, arsenic disulphide (As_2S_2) precipitated, and a solution of a thioarsenite formed. On fusing the trisulphide with sodium carbonate, arsenic sublimes and the residue contains an arsenate and thioarsenate. Arsenic also sublimes when the sulphide is fused with sodium carbonate and potassium cyanide: it is said that none then remains in the residue.

Arsenious sulphide dissolves in an alkali polysulphide, e.g. yellow ammonium sulphide $(\text{NH}_4)_2\text{S}_2$ to form a thioarsenate, also formed when a thioarsenite is digested with sulphur: $\text{AsS}_3 + \text{S} = \text{AsS}_4$. On acidifying, a yellow precipitate is formed which has been described as the pentasulphide or as a mixture of the trisulphide and sulphur. Arsenic trisulphide and sulphur or arsenic pentasulphide when digested with alkali hydroxide form salts containing both oxygen and sulphur: e.g. $\text{Na}_3\text{AsO}_3\text{S}, 12\text{H}_2\text{O}$; K_3AsOS_3 ; $\text{Na}_2\text{HAsO}_3\text{S}, 8\text{H}_2\text{O}$; $\text{Na}_3\text{AsO}_2\text{S}_2, 11\text{H}_2\text{O}$:
$$\text{As}_2\text{S}_5 + 6\text{KOH} = \text{K}_3\text{AsS}_4 + \text{K}_3\text{AsO}_3\text{S} + 3\text{H}_2\text{O}.$$

These are colourless and are decomposed by acids into arsenic acid and free sulphur or arsenic trisulphide. The thioarsenates are soluble and crystalline, e.g. $\text{Na}_3\text{AsS}_4, 8\text{H}_2\text{O}$, $(\text{NH}_4)_3\text{AsS}_4$. By the action of sodium sulphide solution on arsenious oxide in the proportions $2\text{Na}_2\text{S} \cdot \text{As}_2\text{O}_3$ a thioarsenate and elementary arsenic are produced.

A subsulphide As_3S is said to be formed as a dark-brown powder by the action of PCl_3 and SO_2 on sodium arsenite solution, or by the action of sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$) on an arsenite or arsenate solution (Scott, 1900).

ANTIMONY

History.—The earliest records mention under various names a substance used as a pigment and for painting the eyebrows. This practice dates from prehistoric times; it was used in Egypt at least as early as 3400 B.C. The black pigment came from Arabia, was called *mestem*, *stimmi*, afterwards *stibi*, and, although usually galena, was sometimes native antimony sulphide Sb_2S_3 , *stibnite*. In IV. Kings ix. 30, the Vulgate translation is: "Porro Jezebel introitu ejus audito, depinxit oculos suos stibio."

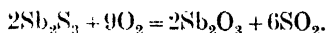
Metallic antimony is easily reduced from stibnite, and a Chaldean vase of 3000 B.C. was found by Berthelot to consist of pure metallic antimony. The metal, not specifically referred to by ancient writers, was probably confused with lead. Constantinus Africanus (c. 1050 A.D.) refers to stibnite as *antimonium*, and the metal was well known to the alchemists. The preparation of metallic antimony and of a number of its compounds is clearly described by Basil Valentine (or Thoele) in the book *Triumph of Chariot of Antimony* (Leipzig, 1604), and antimony compounds were used

in medicine by Paracelsus. The Arabic name for finely-powdered stibnite, *al kohl*, was applied by Paracelsus to the "quintessence," and thence to spirit of wine—*alcohol*.

Occurrence.—Metallic antimony is found in Sweden, Borneo, Queensland, etc.; the oxides Sb_2O_3 (*valentinite* and *senarmonite*) and Sb_2O_4 (*cervantite*) occur only sparingly, and the only important ore is the sulphide Sb_2S_3 , *stibnite*, density 4.64, found in large quantities in China (Hunan province), and less abundantly in Mexico, Bolivia, Peru, Czechoslovakia, Yugoslavia, etc. It is found in black or grey crystals (often radiating needles) or as compact masses. The ores are difficult to concentrate, but flotation can be used.

Metallurgy.—In the preparation of antimony stibnite is first *liquated*, i.e. heated so that the readily fusible sulphide of antimony flows away from the rock. The sulphide is then reduced by heating with iron and a little salt in plumbago crucibles: $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS}$. The metal (*regulus of antimony*) melts and collects below the slag.

The sulphide may also be carefully roasted in a reverberatory furnace to form *antimony dioxide* Sb_2O_3 . At higher temperatures *antimony trioxide* Sb_2O_3 sublimes:



The antimony oxides are mixed with charcoal and sodium carbonate and heated to redness, when reduction occurs: $\text{Sb}_2\text{O}_3 + 3\text{C} = 2\text{Sb} + 3\text{CO}$. The regulus is purified by fusing with sodium carbonate and a little nitre, and then crystallises on cooling, with beautiful star-shaped or fern-like forms on the surface (*star antimony*).

Oxide ores may be dissolved in hydrochloric acid and the antimony precipitated from the solution of antimony trichloride by iron: $2\text{SbCl}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeCl}_2$.

Antimony is precipitated as a fine black powder by zinc from a solution of the trichloride; this powder is used in covering plaster casts to give them the appearance of steel.

Pure antimony is made from the pure pentoxide (prepared by the hydrolysis of recrystallised chlorantimonic acid) by fusing with potassium cyanide or heating in a current of hydrogen.

When a piece of zinc is laid on a piece of platinum foil in an acidified solution of an antimony compound a black stain of antimony deposits on the platinum. If a tin salt is present metallic tin is deposited on the zinc.

Properties.—Antimony is a silver-white lustrous metal, density 6.67, which is brittle and easily powdered. From the fused metal, on slow cooling, large obtuse rhombohedral crystals are formed, but after rapid cooling the metal has a granular structure. The fused metal (m. pt.

630°) expands slightly on solidification. Antimony boils at 1380°. The vapour densities at 1572° and 1640° correspond with the molecular weights 310 and 284, respectively, intermediate between Sb_3 and Sb_2 , perhaps $Sb_4 \rightleftharpoons 2Sb_2$; the freezing points of solutions in lead and cadmium correspond with Sb_2 and Sb , respectively.

Antimony is a poor conductor of heat and electricity; it is diamagnetic.

Antimony is unchanged in air and is not acted upon by water or dilute acids. It decomposes steam at a red heat and is oxidised by concentrated nitric acid, giving oxides of nitrogen and a white powder of hydrated antimony pentoxide. The *pure* metal does not dissolve in concentrated hydrochloric acid in absence of oxygen, but the commercial metal dissolves on heating. Antimony is attacked by hot concentrated sulphuric acid forming the sulphate $Sb_2(SO_4)_3$, and it dissolves readily in aqua regia forming a solution of the pentachloride $SbCl_5$.

When strongly heated in air antimony burns, evolving white fumes of the trioxide Sb_2O_3 . A bead of antimony when heated on charcoal before the blowpipe continues to burn when the flame is removed, and if dropped on a piece of paper turned up at the edges the bead breaks up into burning globules, which disperse and leave curious charred tracks on the paper. Antimony burns brilliantly in oxygen, even in complete absence of moisture. It also ignites spontaneously in chlorine.

Allotropic forms of antimony.—Unstable allotropic forms of antimony are known. **Yellow** or α -antimony is formed by the action of ozonised oxygen on liquid stibine SbH_3 at -90° . It is amorphous and is slightly soluble in carbon disulphide. Yellow antimony is very unstable and passes readily above -90° into **black antimony**, an amorphous black powder, density 5.3, formed directly from liquid stibine and oxygen at -40° . Black antimony oxidises spontaneously in air and on warming forms ordinary antimony, with evolution of heat. **Amorphous antimony** was obtained by Gore (1854) by the slow electrolysis of a concentrated solution of the trichloride in hydrochloric acid with a platinum wire cathode and an antimony anode. The metal deposited on the cathode resembles polished graphite, and has an average density of 5.78. When scratched it is explosively converted into ordinary antimony with evolution of heat and fumes of $SbCl_3$, which it always contains to the extent of 4–12 per cent. At 200° it explodes violently. Amorphous antimony can be kept under water, but if this is heated to 75° the antimony undergoes change with a hissing noise.

Alloys of antimony.—Antimony is a constituent of several important alloys. A mixture of 15 parts of antimony and 85 of lead is *hard lead* or *antimonial lead*, used for stopcocks for sulphuric acid. The most important alloys are with lead and tin, used for printers' type; metal type containing antimony is referred to by Basil Valentine as in common use in 1600. These alloys expand on solidification. The

definite compound $SbCu_2$ is a beautiful purple alloy called *regulus of Venus*.

	Pb	Sb	Sn	Cu	Zn	Bi
Type metal -	- 60	30	10			
Linotype metal -	- 83.5	13.5	3			
Monotype metal -	- 80	15				
Britannia metal		10.4	85.7	1.0	2.9	
Pewter - -		7.1	89.3	1.8		1.8
Anti-friction bearing metal	80	8	12			

$SbCu_2$ with a close-packed hexagonal structure, and many other intermetallic compounds, are known. Antimony forms *antimonides* with alkali metals, Li_3Sb , Na_3Sb , $NaSb$, etc.

COMPOUNDS OF ANTIMONY

Antimony forms two series of compounds, the *antimonous compounds* SbX_3 in which it is 3-valent, and the *antimonic compounds* SbX_5 in which it is 5-valent. Both are stable. The halogen compounds are covalent (although the fluoride forms a conducting solution) and there is little tendency to form salts with oxyacids, the sulphate $Sb_2(SO_4)_3$ being the only one well-defined. The oxides Sb_2O_3 and Sb_2O_4 are amphoteric, but Sb_2O_5 is decidedly acidic. An oxide Sb_2O_4 , which may be $(Sb^{III}O)(Sb^{V}O_3)$, and a chloride $SbCl_4$ in solution, forming stable complex salts, e.g. Rh_2SbCl_6 , are known.

Antimony hydride.— Antimony and hydrogen do not combine directly but the hydride SbH_3 , or *stibine* is formed mixed with hydrogen when a solution of an antimony salt is added to zinc and dilute sulphuric acid (L. Thompson, 1837; Pfaff, 1837) i.e. by the action of nascent hydrogen. The gas burns with a grey flame, evolving white fumes of antimony trioxide. A black stain of antimony is deposited on a cold porcelain dish held in the flame and on both sides of the heated spot on passing the gas through a heated glass tube (arsenic is deposited from arsine only on the side furthest from the generating flask): $2SbH_3 = 2Sb + 3H_2$.

To distinguish the antimony from the similar but brighter arsenic mirror, three spots are formed on the dish, which are treated as follows :

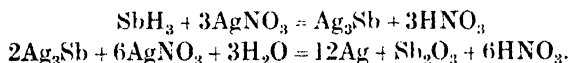
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| <p>(1) Moisten with a solution of bleaching powder :</p> <p>As dissolves :</p> $5Ca(OCl)_2 + 6H_2O + As_4 = 5CaCl_2 + 4H_3AsO_4$ <p>Sb is insoluble.</p> | <p>(2) Moisten with a concentrated solution of tartaric acid :</p> <p>As is insoluble.</p> <p>Sb dissolves forming $(SbO)_2C_4H_4O_6$.</p> | <p>(3) Moisten with yellow ammonium sulphide and evaporate :</p> <p>As gives a yellow residue of As_2S_3.</p> <p>Sb gives an orange residue of Sb_2S_3.</p> |
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A good yield of stibine is obtained by dropping a solution of antimony trichloride in 1 : 1 hydrochloric acid into a flask containing zinc and dilute

hydrochloric acid, or by the action of dilute sulphuric acid on an alloy of equal weights of zinc and antimony. *Pure stibine* is prepared by acting with hydrochloric acid on an alloy of magnesium with 33 per cent of antimony, washing the gas with water, drying with calcium chloride and phosphorus pentoxide, and passing through a tube cooled in liquid air. White solid stibine (m.pt. -88° , b.pt. -17°) is formed. On warming this evolves pure stibine, which may be collected over mercury and is fairly stable when dry.

Stibine is fairly soluble in water and very soluble in carbon disulphide. It has an unpleasant smell and is poisonous. It is attacked by air or oxygen, forming water and antimony, and decomposes into its elements when moist, or with explosion when heated or sparked, or sometimes spontaneously, as it is endothermic. The density is slightly higher than corresponds with SbH_3 .

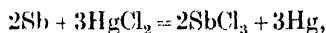
Hydrogen containing stibine gives a black precipitate with silver nitrate solution and the filtrate is free from antimony, whilst with arsine the filtrate contains all the arsenic. The precipitate first formed is silver antimonide Ag_3Sb , but this is rapidly decomposed by excess of silver nitrate into a black mixture of silver, antimony trioxide and a little antimony (Lassaigne, 1840):



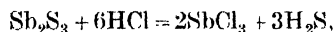
If this precipitate is warmed with hydrochloric acid, the filtrate gives with H_2S an orange-red precipitate of Sb_2S_3 .

Antimony halides.—Covalent halogen compounds of the type SbX_3 are formed with all the halogens, SbX_5 only with fluorine and chlorine.

Antimony trichloride SbCl_3 is formed by heating excess of antimony in chlorine, by distilling antimony with mercuric chloride:



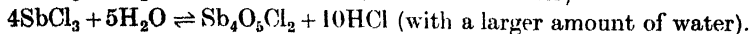
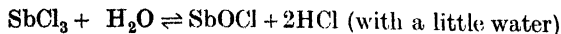
or by dissolving stibnite in hot concentrated hydrochloric acid:



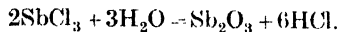
and distilling the solution, when hydrochloric acid comes over first and then antimony trichloride, which solidifies in the receiver as a soft white crystalline mass of *butter of antimony*, m. pt. 73.2° , b. pt. 223.2° .

Fused SbCl_3 is a poor conductor of electricity. The vapour density and the elevation of boiling point in solution in ether correspond with SbCl_3 . Antimony trichloride is decomposed by water with deposition of white basic chlorides. It forms a clear solution with hydrochloric acid. Complex salts, e.g. NaSbCl_4 and K_2SbCl_5 , are formed with metallic chlorides, and it forms crystalline chloroantimonous acid $\text{HSb}_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ with concentrated hydrochloric acid.

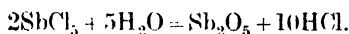
Antimonous oxychloride is precipitated as a white powder when a solution of the trichloride in hydrochloric acid is poured into water. The composition of the precipitate (*powder of Algaroth*) varies with the dilution, but two definite oxychlorides are known :



On heating the oxychloride with water in a sealed tube at 150° , or boiling with sodium carbonate solution, antimony trioxide is formed :



Antimony pentachloride SbCl_5 , discovered by Rose in 1825, is formed when antimony burns in excess of chlorine or by the action of chlorine on antimony trichloride. It is a heavy yellow fuming liquid solidifying in a freezing mixture, m. pt. 3° . The vapour is somewhat dissociated at the boiling point of 150° : $\text{SbCl}_5 \rightleftharpoons \text{SbCl}_3 + \text{Cl}_2$, but under reduced pressure the density corresponds with SbCl_5 . With ice-cold water, two crystalline hydrates are formed, $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ (soluble in chloroform) and $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$ (insoluble in chloroform), but hot water decomposes the pentachloride with formation of hydrated antimony pentoxide :



With concentrated hydrochloric acid antimony pentachloride forms a fairly stable crystalline chlorantimonic acid $2\text{HSbCl}_6 \cdot 9\text{H}_2\text{O}$, which may also be prepared by passing chlorine into a solution of antimony trichloride in hydrochloric acid, and then adding excess of concentrated hydrochloric acid. Numerous salts derived from H_3SbCl_8 , H_2SbCl_7 and HSbCl_6 are known.

A compound SbCl_4 is indicated on the freezing-point diagram of SbCl_5 and Cl_2 (Biltz and Jeep, 1927). Antimony pentachloride combines with many chlorides, oxides, salts, organic compounds, iodine chloride ($\text{SbCl}_5 \cdot 2\text{ICl}$ and $\text{SbCl}_5 \cdot 3\text{ICl}$), sulphur tetrachloride ($\text{SbCl}_5 \cdot \text{SCl}_4$), etc.

The brown liquid formed by the action of chlorine on SbCl_3 appears to contain **antimony tetrachloride** SbCl_4 or an acid $\text{H}_2\text{Sb}^{\text{IV}}\text{Cl}_6$. Many stable dark-coloured salts, e.g. Rb_2SbCl_6 , corresponding with this acid, are known, and as they are isomorphous with corresponding stannic, plumbic and platinum compounds they probably contain quadrivalent antimony (Weinland, 1905).

Antimony tribromide SbBr_3 , white deliquescent needles, formed from the elements, is decomposed by water to the oxybromides SbOBr and $\text{Sb}_4\text{O}_4\text{Br}_2$. The pentabromide is not known but bromantimonic acid $\text{HSbBr}_6 \cdot 3\text{H}_2\text{O}$ is formed in dark-red, almost black, crystals from a solution of SbBr_3 and bromine in concentrated hydrobromic acid, and salts of it are known (Weinland, 1903).

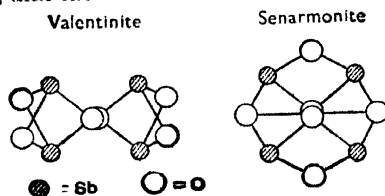
Antimony tri-iodide SbI_3 is formed by warming powdered antimony with a solution of iodine in carbon disulphide and separates in red plates on

evaporation. Two other greenish-yellow forms are described. The vapour of SbI_3 is scarlet. On hydrolysis $\text{Sb}_4\text{O}_5\text{I}_2$ is formed as a yellow powder.

Antimony trifluoride SbF_3 is obtained by distilling antimony with mercuric fluoride, or by dissolving the trioxide in hydrofluoric acid and evaporating. It is not decomposed by water. **Potassium fluorantimonite** K_2SbF_6 is prepared by dissolving Sb_2O_3 in a solution of KF in HF , and is used in calico-printing.

Oxides of antimony.—Antimony forms three oxides, Sb_2O_3 , Sb_2O_4 and Sb_2O_5 , which are stable but are easily reduced by heating with hydrogen or carbon.

Antimony trioxide or *antimonous oxide* Sb_2O_3 or Sb_4O_6 occurs native as *senarmonite*, octahedral, density 5.2, with a diamond lattice like that of As_4O_6 (p. 858), and the commoner rhombic *valentinite*, density 5.67.



Antimony trioxide is formed as a white powder (*flowers of antimony*) by burning antimony in air and (mixed with some Sb_2O_4) by roasting stibnite, also by digesting the oxychlorides SbOCl or $\text{Sb}_4\text{O}_5\text{Cl}_2$ with sodium carbonate solution, and by passing steam over red-hot antimony. A hot solution in sodium carbonate deposits both forms. Antimony trioxide becomes yellow on heating and pale buff on cooling, melts at 656° and boils at 1560° , the vapour density corresponding with Sb_4O_6 . It is almost insoluble in water but is soluble in hot concentrated sulphuric acid, and on cooling crystalline **antimony sulphate** $\text{Sb}_2(\text{SO}_4)_3$ deposits. Antimony trioxide dissolves readily in dilute hydrochloric acid forming SbCl_3 , in tartaric acid, and in alkali solutions forming **metantimonites**, e.g. NaSbO_2 (derived from a hypothetical HSbO_2) which are hydrolysed by water.

Sodium metantimonite is sparingly soluble and crystallises in glittering octahedra as $\text{NaSbO}_2 \cdot 3\text{H}_2\text{O}$; **potassium metantimonite** KSb_3O_5 , obtained by boiling antimonous oxide with potassium hydroxide solution, is readily soluble. Supposed antimonous acids are probably colloidal hydrated oxide.

Antimony trioxide is used in white paints and enamels, but there is a danger that it may be dissolved from these by dilute acids and cause poisoning.

Antimony tetroxide Sb_2O_4 occurs as *cervantite* and is obtained as a white powder by heating the trioxide in air at 700° – 910° . At higher temperatures it decomposes into trioxide. Impure Sb_2O_4 is obtained

as a fused mass by roasting stibnite and is called *glass of antimony*; this contains the tetroxide and unchanged stibnite and is used in colouring glass and porcelain yellow. Antimony tetroxide on fusion with alkalis forms salts called *hypoantimonates*, derived from a hypothetical acid $\text{H}_2\text{Sb}_2\text{O}_5$. The potassium salt $\text{K}_2\text{Sb}_2\text{O}_5$ is sparingly soluble in cold but easily in hot water; if the solution is mixed with hydrochloric acid, $\text{K}_2\text{Sb}_4\text{O}_9$ is precipitated.

Antimony pentoxide Sb_2O_5 is a yellow powder obtained by gently heating the solid formed by the repeated evaporation of antimony with concentrated nitric acid. Above 440° it decomposes into Sb_2O_4 , and when prepared as described always contains a little lower oxide. A stable intermediate oxide Sb_6O_{13} is formed at 430° .

Antimony pentoxide is almost insoluble but reddens litmus. Various *antimonic acids* described are of indefinite composition, but a compound $3\text{Sb}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ or $\text{H}_5\text{Sb}_3\text{O}_{10}$ is shown on the dehydration curve and is formed by heating the hydrated oxide with water under pressure. The pentoxide is acidic and forms salts called *antimonates*.

When antimony pentachloride is precipitated with hot water, or the trichloride or one of the lower oxides treated with nitric acid, the residue after washing and heating at 100° corresponds in composition with *pyroantimonic acid* $\text{H}_4\text{Sb}_2\text{O}_7$. At 200° this is said to form *metantimonic acid* HSbO_3 . *Orthoantimonic acid* H_3SbO_4 is said to be formed by precipitating potassium antimonate with dilute nitric acid and drying over sulphuric acid in a desiccator. The existence of these acids is doubtful.

When a mixture of powdered antimony and potassium nitrate is thrown in portions into a red-hot crucible and the product extracted with warm water, a white residue of potassium antimonate remains, which dissolves slowly in boiling water. Dilute nitric acid precipitates from the solution a hydrated antimony pentoxide, which forms pure antimony pentoxide on heating gently. Hydrated antimony pentoxide is also formed by the action of hot water on antimony pentachloride, and by oxidising the trioxide in presence of water with chlorine, iodine, or potassium dichromate; with bromine, nitric acid, or a mixture of potassium chlorate and hydrochloric acid, the oxidation is incomplete.

A solution of potassium antimonate on evaporation forms a gum readily soluble in warm water. The solution gives with sodium salts a white amorphous precipitate which rapidly forms crystalline *sodium antimonate*, sparingly soluble (1 in 350) in cold water and almost insoluble in alcohol. It is one of the least soluble sodium salts. Lithium and ammonium salts are also precipitated. A corresponding potassium salt is formed by oxidising potassium antimonite with permanganate and evaporating the filtrate. Lead antimonate is the pigment *Naples yellow*.

The alkali antimonates were called metantimonates by Fromy (1844), and Jander (1926) also formulates the sodium salt as $\text{NaSbO}_3 \cdot 3\text{H}_2\text{O}$. The crystalline lithium salt has the composition corresponding with $\text{LiSbO}_3 \cdot 3\text{H}_2\text{O}$. The precipitated sodium salt when dried at 100° has a similar composition but has also been formulated as an acid pyroantimonate $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$. The electrical conductivities of potassium antimonate and Ostwald's rule (p. 300) show that antimonie acid is monobasic, which would agree with the metantimonate formula or with an acid orthoantimonate $\text{KH}_2\text{SbO}_4 \cdot 2\text{H}_2\text{O}$. Pauling (1933), however, pointed out that all the results would agree with the formula $\text{MSb}(\text{OH})_6$ (where $\text{M} = \text{Li}, \text{Na}$ or K), analogous to that of the stannates (p. 831) $\text{M}_2\text{Sn}(\text{OH})_6$, and this is confirmed by the crystal structure found by X-rays.

Antimony pentoxide is an oxidising agent: when dissolved in cold hydrochloric acid it forms the pentachloride and on adding an iodide the iodine liberated may be titrated: $\text{SbCl}_5 + 2\text{KI} = \text{SbCl}_3 + 2\text{KCl} + \text{I}_2$.

Antimony sulphides.—The best known sulphide of antimony, antimony trisulphide Sb_2S_3 occurs as *stibnite*. By precipitating a solution of antimony trichloride in dilute hydrochloric acid with hydrogen sulphide, a red amorphous sulphide, density 4.28, is formed, which if dried at 100° and heated in carbon dioxide at 200° gives off some free sulphur and forms the *greyish-black* rhombic crystalline modification, density 4.65. The red form is used as a pigment (*antimony vermilion*) and in vulcanising rubber, red varieties of which contain it. It is also formed by heating a solution of the trichloride with sodium thiosulphate. If heated at 850° in a stream of nitrogen and the vapour rapidly cooled, lilac-coloured globules of density 4.278 are formed. The red precipitate is insoluble in dilute acids but dissolves in hot concentrated hydrochloric acid (arsenic sulphide is almost insoluble). Colloidal Sb_2S_3 is formed as an orange-red liquid by adding a 0.5 per cent solution of tartar emetic to hydrogen sulphide water.

Antimony trisulphide is reversibly reduced by heating in hydrogen. $\text{Sb}_2\text{S}_3 + 3\text{H}_2 \rightleftharpoons 2\text{Sb} + 3\text{H}_2\text{S}$. A mixture with nitre and sulphur is used as *blue fire* in pyrotechny, and in making matches. Sb_2S_3 dissolves in alkali sulphides and hot concentrated solutions of alkalis and alkali carbonates. On dilution, a red mixture of Sb_2O_3 and Sb_2S_3 (*kermes mineral*) is precipitated. The solutions and the dark-coloured masses (*livers of antimony*) formed by fusing Sb_2S_3 with alkali sulphides contain thioantimonites derived from hypothetical acids H_3SbS_3 , $\text{H}_2\text{Sb}_4\text{S}_7$ and HSbS_2 , and some can be obtained crystalline, e.g. pale-yellow $\text{Na}_3\text{SbS}_3 \cdot 3\text{H}_2\text{O}$, red KSbS_2 , red $\text{Na}_2\text{Sb}_4\text{S}_7 \cdot 2\text{H}_2\text{O}$. Precipitated Sb_2S_3 is insoluble in warm ammonium carbonate solution (As_2S_3 is soluble).

Antimony pentasulphide Sb_2S_5 is formed as a red precipitate on adding saturated hydrogen sulphide solution to a cold solution of Sb_2O_5 containing 10–20 per cent of free hydrochloric acid (Bunsen, 1878). It dissolves in

Antimony pentoxide may be determined by the reaction :



BISMUTH

History.—Metallic bismuth may have been known in antiquity but confused with tin and lead. Agricola (who says it was unknown to the ancients) describes it in his *Bermannus* (1530) under the name of *bisemutum* ; in his *de natura fossilium* (1546) he calls it *plumbum cinereum*. Libavius in his *Commentariorum chymicorum*, 1606, mentions it, noting that it was used to soften tin. The name is supposed to have been derived from the German *wis mat* (white mass), or *wiesen* (a meadow), given to it by the old miners on account of its reddish colour. Pott (1739) and later Bergman investigated its compounds, some of which had been used by Paracelsus for medicinal purposes. The basic nitrate—“bismuth subnitrate,” $\text{Bi}(\text{OH})_2\text{NO}_3$, discovered by Libavius, is still used in medicine in diarrhoea and cholera. This substance, known as *pearl white*, was introduced by Lemery as a cosmetic, although it acts injuriously on the skin, as Lemery himself points out. It has now been replaced by zinc oxide or starch.

Occurrence.—Bismuth occurs *native* with lead, silver and cobalt ores, as the oxide Bi_2O_3 *bismite* or *bismuth ochre*, the sulphide Bi_2S_3 *bismuthinite* or *bismuth glance*, and the basic carbonate $(\text{BiO})_2\text{CO}_3$ *bismuthite* or *bismuth spar*. The most important source is Bolivia ; much is extracted from lead ores in Canada and India, and China, Saxony, and Australia are noteworthy sources.

Metallurgy.—The metal is obtained from native bismuth by liquation, viz. heating in sloping iron tubes when the fusible bismuth (m. pt. 271°) flows away. Oxide and carbonate ores are dissolved in hydrochloric acid and the solution of BiCl_3 either poured into water to precipitate BiOCl or reduced to bismuth by iron. Sulphide ores are roasted and the oxide reduced by carbon, iron, and a flux : the temperature is kept fairly low as the oxide is volatile.

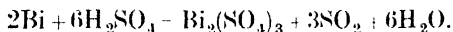
Flue dusts from lead, copper and tin ores, and anode slimes from copper and lead refining, are worked for bismuth. The metal is refined by electrolysis in bismuth chloride and hydrochloric acid in a similar way to copper (p. 721). Very pure bismuth is made by recrystallising the nitrate from a solution containing a large excess of concentrated nitric acid, heating the nitrate to form the oxide, and reducing this by heating with potassium cyanide.

Refined commercial bismuth is 99.0 to 99.9 per cent pure and for making pharmaceutical products must be free from lead and arsenic. *Precipitated bismuth* is a dull-grey powder formed by reducing a solution of BiCl_3 in hydrochloric acid by hypophosphorus acid, and a colloidal solution can be obtained.

Properties.—Bismuth is reddish-white, density 9.80, brittle and easily powdered, and is a poor conductor of heat and electricity. It is strongly diamagnetic. Large obtuse rhombohedra resembling cubes, usually covered with a superficial film of oxide showing green iridescent colours, are formed when the fused metal is cooled. A trace of tellurium alters the appearance and properties of bismuth. Bismuth and its alloys with other metals, which have very low melting points, expand on solidification, and the alloys are used as stereo-metal in printing.

Wood's fusible metal (m. pt. 71°) contains 4 bismuth + 2 lead + 1 tin + 1 cadmium. **Rose's metal** (m. pt. 93.75°) 2 bismuth + 1 lead + 1 tin, and **Lipowitz' alloy** (m. pt. 60°-65°) 15 bismuth + 8 lead + 4 tin + 3 cadmium. Alloys of lead, bismuth and tin, melting slightly above 100°, are used in the construction of automatic sprinklers; when the fusible metal plug is melted water is discharged over the fire. Less fusible alloys are used as safety plugs in boilers.

Bismuth boils at 1450° giving a green vapour, the density of which between 1600° and 1700° indicates partial dissociation: $\text{Bi}_2 \rightleftharpoons 2\text{Bi}$, which is complete at 2000°. It volatilises appreciably at lower temperatures (at 292° in vacuum). The metal is unchanged in dry air and is slowly attacked by water only in presence of oxygen. When fused it slowly oxidises in air, and when strongly heated burns with a bluish-white flame, forming brown fumes of Bi_2O_3 . Pyrophoric bismuth is formed on heating the mellitate under reduced pressure. Bismuth decomposes steam slowly when strongly heated, liberating hydrogen. It does not dissolve in dilute sulphuric or hydrochloric acid in absence of oxygen, but nitric acid dissolves it forming the nitrate $\text{Bi}(\text{NO}_3)_3$. It readily dissolves in aqua regia, forming the chloride BiCl_3 . Boiling concentrated sulphuric acid converts it into the sulphate $\text{Bi}_2(\text{SO}_4)_3$, sulphur dioxide being evolved:



Bismuth compounds.—Bismuth is more electropositive than the other elements in its group, and its chemical properties are intermediate between those of lead and antimony. The chloride BiCl_3 , although easily fusible and volatile and soluble in organic solvents, is an electrolyte when fused, and stable oxysalts such as the nitrate, sulphate and basic carbonate are known. Many salts with organic acids are soluble in benzene. There is a marked tendency to form basic salts, usually formulated as containing the univalent *bismuthyl radical* $-\text{Bi}=\text{O}$. These (unlike the antimonyl compounds) are insoluble in tartaric acid. Unlike antimony, bismuth has little tendency to show a higher valency, all the stable compounds being of trivalent bismuth, although higher oxides contain 4, 5 or possibly 6-valent bismuth. The *bismuthous com-*

pounds, containing bivalent bismuth, were formerly regarded as mixtures of metal and tervalent compounds.

What was regarded as black bismuth monoxide BiO is precipitated by adding a bismuth salt to a solution of sodium stannite (stannous chloride with excess of sodium hydroxide), often accompanied by a white precipitate of bismuth or stannous hydroxide, and hence the reaction, which is used in the identification of bismuth (or stannous) salts, is called the "magpie test." Bismuth monoxide BiO is formed as a black powder, unchanged at 300° , by oxidising a solution of Na_3Bi in liquid ammonia with oxygen (Watt and Moore, 1948): $4\text{Na}_3\text{Bi} + 6\text{NH}_3 + 5\text{O}_2 = 4\text{BiO} + 6\text{NaOH} + 6\text{NaNH}_2$.

Bismuth hydride.—When the hydrogen evolved by the action of 4N sulphuric or hydrochloric acid on an alloy of equal parts of bismuth and magnesium is passed through a heated tube, it deposits a brown mirror of bismuth in front of the heated spot and a fainter one behind, suggesting that a trace of a gaseous hydride (BiH_3 ?), which is very unstable, is formed. It is absorbed to some extent by water and is more soluble in dilute alkali, indicating that it is acidic rather than basic. Thorium-C, an isotope of bismuth, when deposited on magnesium, gives a radioactive gaseous hydride on solution in acid.

Bismuth halides.—All the halogen compounds of bismuth are formed by the action of halogens on the metal: fluorine does not react easily even at a red heat, and the other halogens react without incandescence on heating. Bismuth fluoride is stable to water but the other halides form basic salts.

Bismuth trifluoride BiF_3 is formed as a white powder, non-volatile at a red heat, on evaporating a solution of bismuth trioxide in hydrofluoric acid. With excess of oxide an **oxyfluoride** BiOF is formed. A white **bismuth pentafluoride** BiF_5 is formed from the trifluoride and fluorine. It sublimes at 550° .

Bismuth trichloride BiCl_3 , is formed as soft white crystals, m. pt. 227° , b. pt. 447° , on passing excess of chlorine over bismuth. Boyle (1663) obtained it by heating bismuth with mercuric chloride: $2\text{Bi} + 3\text{HgCl}_2 = 2\text{BiCl}_3 + 3\text{Hg}$. Its vapour density corresponds with the formula BiCl_3 . The trichloride is also formed by dissolving bismuth in aqua regia, evaporating (when crystals of $\text{BiCl}_3 \cdot 2\text{H}_2\text{O}$ are deposited) and distilling. The solution in concentrated hydrochloric acid deposits at 0° crystals of chlorobismuthous acid $\text{H}[\text{Bi}_2\text{Cl}_7] \cdot 3\text{H}_2\text{O}$, stable at the ordinary temperature. Salts of H_2BiCl_5 , HBiCl_4 and HBi_2Cl_7 , and the compounds $\text{BiCl}_3 \cdot \text{NOCl}$ and $2\text{BiCl}_3 \cdot \text{NO}$, are known.

A solution of bismuth chloride when poured into water gives a white precipitate of **bismuth oxychloride** (or *bismuthyl chloride*) BiOCl which can be obtained crystalline. This is deposited when any bismuth salt is added to a solution of sodium chloride; it resembles silver chloride in turning grey and losing chlorine on exposure to light.

The black dichloride BiCl_2 , formed on heating BiCl_3 with excess of bismuth, or by heating bismuth with calomel at 250° , may be a mixture of BiCl_3 and bismuth.

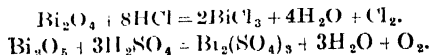
Bismuth tribromide BiBr_3 , m. pt. 215° , b. pt. 453° , is formed from the elements in golden-yellow crystals, decomposed by water into white BiOBr . **Bismuth tri-iodide** BiI_3 , m. pt. 412° , is a black powder obtained by adding bismuth oxide to a solution of iodine in stannous chloride saturated with HCl . It is slowly decomposed by water, forming the red oxyiodide BiOI . Bismuth iodide dissolves in hydriodic acid, forming iodobismuthous acid $\text{HBiI}_4 \cdot 4\text{H}_2\text{O}$, and in alkali iodides, forming red crystalline salts, e.g. KBiI_4 .

Bismuth oxides.—The only well-defined oxide of bismuth is **bismuth trioxide** Bi_2O_3 , a pale-yellow powder (greenish-grey when not quite pure). It is formed by heating the metal, hydroxide, basic carbonate, or nitrate to redness in air. It melts at a red heat and solidifies at 820° . The solid changes at 701° with evolution of heat into a second form, consisting of greenish-yellow crystals. A third form obtained in yellow needles by heating the oxide in a porcelain crucible to the melting point probably contains silica. Bismuth trioxide is used in producing an iridescent white glaze on porcelain. When mixed with other oxides and fused on the surface of glass, it is used in making stained glass: a mixture of Bi_2O_3 and Cr_2O_3 fused on glass gives a lemon-yellow colour. Bismuth oxide is also used to make some kinds of optical glass.

Bismuth hydroxide $\text{Bi}(\text{OH})_3$ is formed as a white gelatinous precipitate, which becomes crystalline, on adding an alkali hydroxide or ammonia to a solution of the nitrate; it is insoluble in excess of alkali unless shaken with *concentrated* sodium hydroxide, or when glycerol is added, but is readily soluble in acids. When heated to 100° it forms $\text{BiO}(\text{OH})$, and at a red heat Bi_2O_3 .

Higher oxides of bismuth are precipitated as reddish-brown powders on adding oxidising agents such as potassium ferricyanide or chlorine to alkaline suspensions of bismuth trioxide. From a suspension in hot dilute alkali, chlorine precipitates a scarlet powder which is principally **bismuth tetroxide** Bi_2O_4 . From the suspension in concentrated alkali, chlorine precipitates also some **bismuth pentoxide** Bi_2O_5 . Both these oxides dissolve in hot nitric acid of density 1.2 with evolution of oxygen. By oxidising with ferricyanide or persulphate in concentrated alkali, a small amount of **bismuth hexoxide** Bi_2O_6 , insoluble in nitric acid, is formed.

The higher oxides lose oxygen on heating and are reduced when warmed with concentrated hydrochloric or sulphuric acids:



The higher oxides of bismuth show *acidic* properties. On fusing bismuth trioxide with potassium hydroxide in air, a brown mass of potassium

bismuthate, perhaps KBiO_3 , is formed; it is hydrolysed by water and hydrated Bi_2O_5 is precipitated. Potassium bismuthate is used as an oxidising agent; with *cold* solutions of manganous salts in dilute nitric acid it gives a purple solution of permanganic acid. In its higher oxides bismuth shows some resemblance to lead.

Normal bismuth carbonate is unknown but white basic bismuth carbonate $(\text{BiO})_2\text{CO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ is precipitated when ammonium carbonate is added to a solution of the nitrate. It loses water at 100° and carbon dioxide at a higher temperature. Bismuth carbonate is given as a "bismuth meal" before X-radiology of the digestive tract, as it is opaque to X-rays.

The most important bismuth salt is bismuth nitrate, obtained in deliquescent crystals $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ by evaporating a solution of the metal, oxide or basic carbonate in warm dilute nitric acid. The solution on pouring into a large volume of water deposits white basic bismuth nitrate or "subnitrate" $\text{Bi}(\text{OH})_2\text{NO}_3$, used in medicine and formerly as a cosmetic. On washing with water this slowly forms $(\text{BiO})_2(\text{OH})\text{NO}_3$. The commercial basic nitrate is $6\text{Bi}_2\text{O}_3 \cdot 5\text{N}_2\text{O}_5 \cdot 8\frac{1}{2}\text{H}_2\text{O}$. Anhydrous $\text{Bi}(\text{NO}_3)_3$ cannot be obtained by heating the crystalline salt, as decomposition occurs, but by drying in vacuum over P_2O_5 for a year $\text{Bi}(\text{NO}_3)_3$ is formed.

By grinding bismuth nitrate crystals with mannitol and adding water a clear solution is obtained. The nitrate can be obtained in solution if dilute nitric acid is added. The basic chloride and nitrate are readily distinguished from the antimony salts by adding a few crystals of tartaric acid and warming. The antimony salts dissolve but the bismuth salts are insoluble.

Bismuth sulphide Bi_2S_3 is obtained in lead-grey crystals by fusing bismuth with sulphur, or as a brownish-black precipitate (solubility 0.2 mgm. per litre) when hydrogen sulphide is passed into a solution of a bismuth salt. The precipitate dissolves in nitric acid and in boiling concentrated hydrochloric acid, but not in alkalis or yellow ammonium sulphide, since it does not (like the sulphides of arsenic, antimony and tin) form thio-salts in this way.

Thio-salts are formed by dissolving bismuth sulphide in concentrated *potassium* sulphide, or by fusion with sulphides. Bi_2S_3 is only sparingly soluble in sodium sulphide. The salts KBiS_2 and NaBiS_2 form fine crystals with a metallic lustre, rapidly oxidised in the air. On diluting the solution of the sodium salt, Bi_2S_3 is reprecipitated.

Bismuth sulphate $\text{Bi}_2(\text{SO}_4)_3$ is obtained as a white amorphous mass by evaporating the metal with hot concentrated sulphuric acid. It forms a sparingly soluble basic sulphate $\text{Bi}_2(\text{OH})_4\text{SO}_4$ on addition of water. On heating, this forms yellow bismuthyl sulphate $(\text{BiO})_2\text{SO}_4$. A double salt $\text{KBi}(\text{SO}_4)_2$ is formed with potassium sulphate.

Sodium thiosulphate with a solution of a bismuth salt gives a clear solution containing sodium bismuth thiosulphate $\text{Na}_3[\text{Bi}(\text{S}_2\text{O}_3)_3]$, which does not react with iodine. The solution quickly decomposes and deposits bismuth sulphide. It gives with potassium salts a sparingly soluble yellow potassium bismuth thiosulphate $\text{K}_3[\text{Bi}(\text{S}_2\text{O}_3)_3] \cdot \frac{1}{2}\text{H}_2\text{O}$, and the reaction may be used in the detection of potassium. On boiling sodium bismuth thiosulphate solution the bismuth is quantitatively precipitated as sulphide: $2\text{Bi}^{+++} + 3\text{S}_2\text{O}_3^{--} + 3\text{H}_2\text{O} = \text{Bi}_2\text{S}_3 + 3\text{H}_2\text{SO}_4$.

Many salts of bismuth with organic acids (salicylate, basic gallate, basic dibromohydroxynaphthoate, hydroxyiodogallate, etc.) and phenols (β -naphthol, pyrogallol, etc.) are used in pharmacy.

The atomic weight of bismuth was found by different methods with discordant results, e.g. 208.05 by Schneider in 1851 from the ratio $2\text{Bi} : \text{Bi}_2\text{O}_3$ and 210.7 by Dumas in 1859 from the analysis of the chloride. The value 209.02 was found by Hönigschmid in 1920 by analysis of the chloride. The valency is found from the atomic heat and the vapour density of the chloride.

VANADIUM

In 1801 Del Rio discovered in a Mexican lead ore a new element which gave coloured salts with acids, but Descotils in 1804 reported that the mineral was lead chromate. Sefström in 1830 discovered in Swedish iron and slags an element which was called *vanadium* (after the Scandinavian goddess Vanadis), and Wohler showed that the Mexican ore is lead vanadate. Berzelius, with a few grams of Sefström's material, prepared a number of compounds of vanadium, which he supposed formed an acidic oxide VO_3 like CrO_3 . In 1867 Roscoe found that the oxide was V_2O_5 , and first prepared the metal, what Berzelius had regarded as vanadium being the oxide VO (which is not reduced by heated potassium) or the nitride VN.

Vanadium is a rare element but is widely distributed. The principal ores are *carnotite* or potassium vanadate $\text{K}_2(\text{VO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$, *vanadinite* $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$ (see p. 360), and especially the impure sulphide *patronite*, found at 17,000 ft. on the Peruvian Andes (and the chief source of vanadium) and North Rhodesia. Small quantities of vanadium are found in clays, rocks, coal, and crude oil (the flue dust from oil burners usually contains some V_2O_5).

Ferrovandium is made from patronite and is used for making steel. Pure vanadium is difficult to obtain, as it readily combines with oxygen, carbon, and nitrogen: it can be prepared by strongly heating a mixture of V_2O_5 , calcium, and calcium chloride in a steel bomb: $\text{V}_2\text{O}_5 + 5\text{Ca} + 5\text{CaCl}_2 = 2\text{V} + 5(\text{CaO}, \text{CaCl}_2)$, and is soft and ductile. Roscoe prepared vanadium by strongly heating vanadium dichloride for several days in a current of very pure hydrogen: $\text{VCl}_2 + \text{H}_2 = \text{V} + 2\text{HCl}$.

The common oxide of vanadium is vanadium pentoxide V_2O_5 , a reddish-yellow sparingly soluble solid, which is an acidic oxide and forms vanadates; salts corresponding with ortho-, pyro-, and meta-vanadic acids, H_3VO_4 , $\text{H}_2\text{V}_2\text{O}_7$, and HVO_3 , are known. Sodium orthovanadate $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$ is isomorphous with the phosphate $\text{Na}_3\text{P}(\text{O}_4)_3 \cdot 12\text{H}_2\text{O}$. The common ammonium vanadate is the metavanadate NH_4VO_3 , which is sparingly soluble. Vanadic acid also forms polyvanadates, derived from the acid $\text{H}_4\text{V}_6\text{O}_{17} = 3\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$.

Vanadium pentoxide dissolves in concentrated sulphuric acid and on dilution a pale-yellow solution is formed. Sulphur dioxide reduces this to a blue solution of **vanadyl sulphate** $VOSO_4$, containing 4-valent vanadium. Magnesium and hydrochloric acid reduce the solution of V_2O_5 to a green solution of **vanadium trichloride** VCl_3 , containing 3-valent vanadium, and prolonged reduction with zinc and dilute sulphuric acid (more rapidly by shaking with zinc amalgam) gives a lavender-coloured solution of **vanadium dichloride** VCl_2 , containing 2-valent vanadium. The solution of V_2O_5 in dilute sulphuric acid gives with hydrogen peroxide a red colour, supposed to be due to **pervanadic acid** HVO_4 .

The oxides VO , V_2O_3 , VO_2 , and V_2O_5 are known. The highest chloride is the **tetrachloride** VCl_4 but there is a **pentafluoride** VF_5 . On passing chlorine over a heated mixture of V_2O_5 and carbon, the yellow liquid **oxychloride** $VOCl_3$ is formed, not decomposed by boiling with sodium. By passing the vapour of $VOCl_3$ mixed with chlorine over heated carbon a red liquid, VCl_4 , is formed. By passing a mixture of VCl_4 vapour and hydrogen through a red-hot tube a peach-blossom coloured sublimate of VCl_3 is formed, and by heating this to redness in nitrogen, apple-green VCl_2 is obtained. Compounds of bi- and trivalent vanadium are powerful reducing agents. In these valency stages vanadium shows analogies with ferrous and ferric iron. V^{II} forms violet $VSO_4 \cdot 7H_2O$ isomorphous with $FeSO_4 \cdot 7H_2O$, and brownish-yellow $K_4V(CN)_6 \cdot 3H_2O$ (cf. potassium ferrocyanide). V^{III} forms $V_2(SO_4)_3$, giving alums $M^{I}V^{III}(SO_4)_2 \cdot 12H_2O$, and $K_3V(CN)_6$ (cf. potassium ferricyanide).

Vanadium pentoxide is used as a catalyst in the oxidation of naphthalene vapour and air to phthalic anhydride, and of sulphur dioxide and air to sulphur trioxide, and vanadium compounds (which are poisonous) are used in making ink, as drying accelerators in paints and varnishes, as insecticides, in photography and medicine, and in glass manufacture.

NIObIUM AND TANTALUM

In 1801 Hatchett discovered in a mineral thought to have come from America and called *columbite* (it perhaps really came from Sweden) a new metal which is called **columbium**. Ekeberg in 1802 discovered in a mineral afterwards called *ytrotantalite* another new metal which he called **tantalum**, since it is not acted upon at all by acids. Wollaston in 1809 thought he had shown that the two metals are the same, but later work by Rose showed that they are different. Rose changed the name columbium to **niobium**, which is the name now used for the element.

The two elements occur together. The chief minerals are *columbite* and *tantalite*, both $Fe(Nb,Ta)O_3$, the first richer in niobium and the second in tantalum. The metals are now extracted from American minerals and are finding uses; tantalum, m.pt. 2850° , is ductile and can be used in radio-valve grids and plates, and niobium, m.pt. 1950° , improves stainless steel. Both metals resist acids, but are oxidised when heated in air and are decomposed by fused alkalis. The carbides of niobium and tantalum are very hard and are used for cutting tools.

Niobium and tantalum form white solid acidic **pentoxides**, Nb_2O_5 and Ta_2O_5 , which form niobates and tantalates. The two **complex fluorides**

K_2TaF_7 (the ion TaF_7^{2-} containing tantalum with a coordination number of 7) and $K_2NbOF_6 \cdot H_2O$ (*potassium fluoxyphosphate*) are used in the separation of the elements by fractional crystallisation, the first being sparingly and the second easily soluble. The chlorides $NbCl_3$ and $TaCl_3$, and $NbCl_5$ and $TaCl_5$ are known, and both metals form the complex acidic compounds $H[Nb_3Cl_7(H_2O)] \cdot 3H_2O$ and $H[Ta_3Cl_7(H_2O)] \cdot 3H_2O$ in which they are bivalent ($3XCl_2, HCl, 4H_2O$).

PROTOACTINIUM

The element **protoactinium** (or *protactinium*) a disintegration product of uranium-Y (p. 401), was separated in appreciable amounts from pitchblende residues by von Grosse. The steady decrease in acidic character in the series V_2O_5 , Nb_2O_5 , and Ta_2O_5 reaches a climax in **protoactinium pentoxide** Pa_2O_5 which is a white solid which is basic and resembles thorium dioxide ThO_2 rather than the other oxides. The metal protoactinium is formed by electron bombardment of Pa_2O_5 on a copper target and is stable in air. The **pentachloride** $PaCl_5$ forms colourless volatile needles.

CHAPTER XLIV

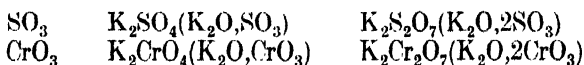
GROUP VI METALS

GROUP VI of the Periodic System (apart from the radioactive element polonium) comprises eight elements :

Sub-Group (b) (Odd Series)					
	O	S	Se	Te	
Atomic number - -	8	16	34	52	
Electron configuration -	2·6	2·8·6	2·8·18·6	2·8·18·18·6	
Density (solid) - -	1·4256	2·1	4·8	6·235	
Atomic volume - -	11·2	15·3	16·5	20·4	
Melting point - -	- 218·4°	112·8°	220·2°	452·5°	
Boiling point - -	- 183°	444·60°	684·8°	1390°	

Sub-Group (a) (Even Series)					
	Cr	Mo	W	U	
Atomic number - -	24	42	74	92	
Electron configuration	2·8·13·1	2·8·18·13·1	2·8·18·32·12·2	2·8·18·32·18·12·2	
Density - - -	7·14	10·2	19·3	18·685	
Atomic volume - -	7·3	9·4	9·5	12·7	
Melting point - -	1840°	2620°	3390°	1150°	
Boiling Point - -	2200°	3700°	5900°	3500°?	

At first sight no obvious resemblances exist between the elements of the odd and even series. The former are non-metals ; the latter are all metals. If we take sulphur as representative of the odd series and chromium of the even series, however, a closer examination of their chemical properties reveals many points of similarity. Both form acidic trioxides RO_3 , the salts of which are isomorphous and have similar formulae :



Both elements form stable oxychlorides RO_2Cl_2 , hydrolysed by water, but there is no chloride of chromium corresponding with S_2Cl_2 . The stable chloride of chromium is $CrCl_3$, corresponding with $FeCl_3$ and $AlCl_3$, and chromium shows many resemblances to aluminium and iron. The metals chromium and iron are similar, and the oxides Al_2O_3 , Cr_2O_3 and Fe_2O_3 are isomorphous. The three metals Al, Cr, Fe, are classed together in the same group in qualitative analysis. The analogy between iron and chromium is also seen in the formation of ferrates, e.g. K_2FeO_4 (red) and chromates, e.g. K_2CrO_4 (yellow). The bivalent chromium compounds CrX_2 resemble the ferrous salts and are strong reducing agents.

Molybdenum and tungsten resemble chromium in their chemical properties: they form acidic trioxides MoO_3 and WO_3 but the salts derived from WO_3 are usually complex and correspond with polyacids such as paratungstic acid $\text{H}_{10}\text{W}_{12}\text{O}_{11}$ ($=12\text{WO}_3 + 5\text{H}_2\text{O}$) and metatungstic acid $\text{H}_2\text{W}_4\text{O}_{13}$ ($=4\text{WO}_3 + \text{H}_2\text{O}$). Ordinary ammonium molybdate is $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ($=3(\text{NH}_4)_2\text{O} + 7\text{MoO}_3$). Uranium differs somewhat from its companions, since its stable salts are derived from a bivalent *uranyl* radical UO_2 . Molybdenum and tungsten form a number of complex acids with phosphoric acid, etc.

Except in the case of oxygen the maximum valency in the group is 6, but lower valencies 2 and 4 are shown in Sub-group *b*, and 2, 3, 4 and 5 in Sub-group *a*, the metals of which are definitely *transitional elements* (p. 431).

They show resemblances to neighbouring elements (V, Mn, Fe, Co, Ni) and the varying valencies arise from the possibility of electrons in the shell below the valency electron shell functioning easily as valency electrons:

Cr	2		8		2·6·5		1
Mo	2		8		18		2 6 5 1
W	2		8		18		32 2·6·4 2
U	2		8		18		32 18 2·6·4 2

Because of their transitional character the metals form strongly coloured compounds which are often paramagnetic.

For the same element the acidic character of the hydroxide increases with the valency: $\text{Cr}^{\text{II}}(\text{OH})_2$ and $\text{Cr}^{\text{III}}(\text{OH})_3$ are basic, $\text{Cr}^{\text{VI}}\text{O}_4\text{H}_2$ or $\text{Cr}^{\text{VI}}\text{O}(\text{OH})_2$ is acidic. In Sub-group *b* the dioxides RO_2 are acidic, forming salts M_2RO_3 . The lower oxides of Sub-group *a* are more basic, and other oxides *e.g.* R_2O_3 related to those of neighbouring transitional elements are known.

The *halides* are predominantly covalent and volatile, although those of lower valencies in Sub-group *b* are either ionic or associated into peculiar groupings. Some of them are hydrolysed by water or alkalis. All the elements form stable covalent oxychlorides $\text{R}^{\text{VI}}\text{O}_2\text{Cl}_2$.

CHROMIUM

History.—A red Siberian mineral now called *crocoisite* described by J. G. Lehmann in 1766 was found by Vauquelin and Klaproth in 1797 to be lead chromate PbCrO_4 , containing the new element chromium. The name chromium (Greek, *chroma* colour) was given to the element because it forms a large number of coloured compounds. Metallic chromium was obtained by Vauquelin by reducing the green oxide Cr_2O_3 with carbon at a white heat.

Occurrence.—Chromium occurs in small amounts in some iron meteorites. The commonest ore is *chromite* or *chrome-ironstone*, ferrous chromite FeCr_2O_4 or $\text{FeO}, \text{Cr}_2\text{O}_3$, a spinel (p. 811). Rarer minerals are *chrome-ochre* Cr_2O_3 and *chromitite* $\text{Fe}_2\text{O}_3, 2\text{Cr}_2\text{O}_3$.

Chromite is mined principally in Greece, Russia, Asia Minor, India, Turkey, Rhodesia and New Caledonia. It is very refractory and is made into chrome bricks for furnace linings or to separate the silica bricks from the magnesia bricks in the lining of the basic-hearth steel furnace. Chromite is the source of chromium compounds and chromium alloys.

Chromium forms three series of compounds :

- (i) the **chromous salts** CrX_2 containing 2-valent Cr, and resembling manganous and ferrous salts ; CrO is strongly basic ;
- (ii) the **chromic salts** CrX_3 containing 3-valent Cr, and resembling ferric salts : Cr_2O_3 is weakly basic and amphoteric ;
- (iii) **chromium trioxide** CrO_3 , containing 6-valent Cr and analogous to sulphur trioxide, strongly acidic and forming **chromates** and **dichromates**.

Metallic chromium.—Chromium is obtained by reducing the green sesquioxide in perfectly dry hydrogen at 1500° or with aluminium in the aluminothermic process (p. 807) : $\text{Cr}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Cr}$.

A tin canister 10 in. by 6 in. is filled with coarsely-powdered fluorspar and a depression 2 in. \times 8 in. made in it by a large test-tube. The mixture of the dry oxide and aluminium powder is pressed into this and the $(\text{BaO}_2 + \text{Mg})$ igniter placed on the top (Fig. 383). The fluorspar is a good heat insulator so that a fused mass is obtained even with small amounts of material. A mixture of aluminium powder with an equal or double weight of calcium turnings, corresponding with the oxygen of the oxide, acts even more effectively than aluminium alone and is used in the case of oxides such as Cr_2O_3 which are reduced with difficulty ; or a mixture of 4 parts Cr_2O_3 , 1 part powdered fused $\text{K}_2\text{Cr}_2\text{O}_7$, and 1.9 parts Al powder, is used.

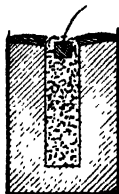


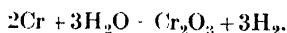
FIG. 383.—Arrangement for thormit reaction.

Pure chromium is obtained by electrolysing a solution of chromic chloride CrCl_3 with a mercury cathode and heating the amalgam in a vacuum to remove mercury. It is also deposited electrolytically in chromium plating. Chromium is deposited (usually on nickel) in *chromium plating* from a hot solution of chromic acid and a little chromic sulphate with a lead anode.

An alloy of iron and chromium called *ferrochrome* is made industrially by reducing chrome ironstone with carbon in the electric furnace and is used in the manufacture of *chrome steel* (steel containing chromium).

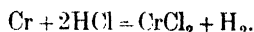
Chrome steel is not attacked by acids. An alloy of chromium, nickel and iron is used for armour plates. *Stainless steel* is ordinary steel with 12 to 14 per cent of chromium and up to 0.7 per cent of nickel. Steels with 17 to 18 per cent of chromium and 7 per cent or more of nickel are not hardened by quenching and have superior corrosion resistance.

Chromium is a malleable metal, silver-white with a bluish tinge, with a high melting point. The pure metal is not very hard, the hardness of the electrodeposited metal being due to the crystal form and to occluded hydrogen. There are three crystalline forms. Chromium burns brilliantly in the oxyhydrogen flame forming the oxide Cr_2O_3 , and decomposes steam at a red heat :



Finely-divided chromium left on heating the amalgam is pyrophoric and combines with atmospheric oxygen and nitrogen. On heating in nitrogen or ammonia it forms the brown or black chromium nitride CrN .

Chromium dissolves slowly in dilute sulphuric and hydrochloric acids especially on heating, forming blue solutions of chromous salts :



The solutions rapidly absorb atmospheric oxygen, forming green solutions of chromic salts :

$$4\text{CrCl}_2 + 4\text{HCl} + \text{O}_2 = 4\text{CrCl}_3 + 2\text{H}_2\text{O}.$$

Hot concentrated sulphuric acid attacks chromium rapidly, sulphur dioxide being evolved. Dilute nitric acid does not dissolve the pure metal and in the concentrated acid it becomes *passive* and is then unattacked by dilute acids. Passivity (due to a film of oxide) is also induced by exposure to air or dipping in chromic acid. It is destroyed by touching the metal under the surface of dilute sulphuric acid with zinc.

CHROMOUS COMPOUNDS

The chromous salts contain 2-valent chromium and are powerful reducing agents. They are formed by dissolving the metal in acids or by reducing chromic salts with nascent hydrogen (zinc and dilute acid) : $\text{Cr}^{+++} + \text{H} = \text{Cr}^{++} + \text{H}^+$. This reaction is reversible and chromous salts in acid solution evolve hydrogen, especially in contact with platinum, although they do not react with pure water.

50 gm. of pure granulated zinc and 10 gm. of finely-powdered potassium dichromate are placed in a flask fitted with a tap funnel and a delivery tube dipping under water (Fig. 384). 200 ml. of concentrated hydrochloric acid mixed with 100 ml. of water are added. A violent reaction occurs, the liquid first becoming green (CrCl_3) and then blue (CrCl_2). The liquid is rapidly passed through an asbestos filter into a saturated solution of sodium acetate (92 gm. of sodium acetate crystals), when red chromous acetate $\text{Cr}(\text{CH}_3\text{CO}_2)_2$ is thrown down. This is fairly stable; it is washed in a closed flask by decantation with water saturated with carbon dioxide.

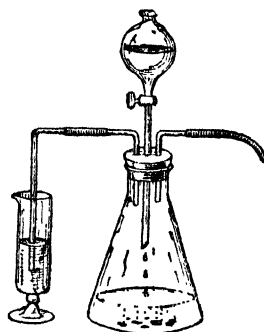


FIG. 384.—Preparation of chromous chloride.

The second part of the preparation is more difficult. The air is expelled from the flask by hydrogen and the solid dissolved in concentrated hydro-

chloric acid. A blue solution of chromous chloride is formed. This is cooled in ice and a current of hydrogen chloride gas is passed in. Chromous chloride hydrate $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ is precipitated in blue needles.

Anhydrous chromous chloride is obtained by heating chromic chloride in hydrogen: $2\text{CrCl}_3 + \text{H}_2 = 2\text{CrCl}_2 + 2\text{HCl}$, or metallic chromium in hydrogen chloride. It forms *white* deliquescent silky needles. The vapour density at high temperatures corresponds with the equilibrium: $\text{Cr}_2\text{Cl}_4 \rightleftharpoons 2\text{CrCl}_2$.

Chromous fluoride CrF_2 , formed by the action of hydrogen fluoride on CrCl_2 , is white and nearly insoluble. **Chromous bromide** CrBr_2 and **chromous iodide** CrI_2 , formed by passing hydrogen over the heated chromic compounds, are white and soluble in water to blue solutions.

Sodium hydroxide added to a solution of a chromous salt in absence of air precipitates brownish-yellow **chromous hydroxide** $\text{Cr}(\text{OH})_2$, which is readily oxidised in air and in the moist state evolves hydrogen: $2\text{Cr}(\text{OH})_2 + 2\text{H}_2\text{O} = 2\text{Cr}(\text{OH})_3 + \text{H}_2$. **Chromous oxide** CrO cannot therefore be obtained by heating the hydroxide; it is formed as a black powder on exposure of chromium amalgam to air.

Chromous carbonate $\text{Cr}(\text{CO}_3)$ is obtained as a grey precipitate on adding alkali carbonate to a solution of a chromous salt. It forms stable red or yellow double carbonates $\text{K}_2\text{Cr}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{Cr}(\text{CO}_3)_2 \cdot 10\text{H}_2\text{O}$.

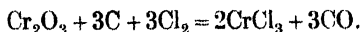
Chromous oxalate $\text{Cr}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ is only sparingly soluble; when moist it has little tendency to take up atmospheric oxygen, and when dry it is the most stable chromous salt.

Chromous sulphate $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ is obtained in fine blue crystals isomorphous with ferrous sulphate by dissolving the acetate or metal in dilute sulphuric acid and cooling the solution. It forms blue double salts, e.g. $\text{K}_2\text{Cr}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The ammoniacal solution of CrSO_4 absorbs acetylene and the aqueous solution absorbs oxygen and nitric oxide.

CHROMIC COMPOUNDS

The chromic salts are stable compounds containing 3-valent chromium and mostly exist in at least two modifications: (i) a *violet* form in hydrated crystals or in solution, the latter containing the chromic ion Cr^{+++} or probably $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$; and (ii) one or more *green* modifications in which part or all of the chromium is present as a complex ion. In the green solutions there is generally hydrolysis. With very weak acids 3-valent chromium forms complex salts in which it exists in very stable anions. Another group of complex compounds are the *ammine* compounds with ammonia, e.g. $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$.

Anhydrous **chromic chloride** is obtained as a sublimate of peach-blossom coloured scaly crystals when chlorine is passed over heated chromium or a mixture of chromic oxide and carbon heated to redness:

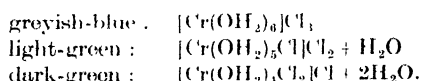


It is also formed by heating the hydrate in hydrogen chloride. The crystals are volatile at 1065° and the vapour density at 1200° - 1300° corresponds with CrCl_3 . At higher temperatures there is dissociation : $2\text{CrCl}_3 \rightleftharpoons 2\text{CrCl}_2 + \text{Cl}_2$. The crystals are almost insoluble in cold water and are not attacked by boiling concentrated sulphuric acid, but readily dissolve in water in presence of a trace of chromous chloride (or a reducing agent such as SnCl_2 or CuCl) giving a green solution.

Three crystalline hydrates of chromic chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are known, all readily soluble in water, viz. two *green* and one *greyish-blue*. The *dark-green* chloride is the common form. It is obtained by dissolving chromic hydroxide in hydrochloric acid or when chromium trioxide is boiled with concentrated hydrochloric acid : $2\text{CrO}_3 + 12\text{HCl} = 2\text{CrCl}_3 + 3\text{Cl}_2 + 6\text{H}_2\text{O}$. The solution is evaporated until its weight corresponds with less water than $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, then made up to this weight and cooled.

The *greyish-blue* chloride is made by dissolving the crude dark-green chloride in its own weight of water, boiling for half an hour under a reflux, cooling below 0° and passing in excess of hydrogen chloride, when it crystallises. The *light-green* chloride is precipitated on adding ether saturated with hydrogen chloride to the filtrate from the greyish-blue chloride and passing in hydrogen chloride at 10° .

In solution the greyish-blue chloride gives three chloride ions, since all the chlorine can be precipitated with silver nitrate. The light-green form gives only two chloride ions and readily loses a molecule of water. The dark-green form gives only one chloride ion precipitated by silver nitrate in presence of a little nitric or sulphuric acid, filtering rapidly, and it readily loses two molecules of water. Werner represented the constitution of the three forms as follows :



The atoms or molecules inside the square brackets are directly co-ordinated (p. 416) with the metal atom and are not ionisable, whereas the radicals outside are ionisable. The number of atoms or molecules co-ordinated with the chromium atom is always six.

Chromic fluoride CrF_3 sublimes in dark-green needles on passing hydrogen fluoride over heated CrCl_3 ; it is sparingly soluble. Small quantities of a brown solid tetrafluoride CrF_4 and a bright-red liquid pentafluoride CrF_5 are formed by the action of fluorine on chromium.

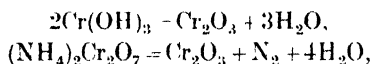
Chromic bromide CrBr_3 (greenish-black) and **chromic iodide** CrI_3 (red) are formed by passing bromine and iodine vapour over heated chromium, and form hydrates $\text{CrBr}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CrI}_3 \cdot 9\text{H}_2\text{O}$.

Chromic nitrate $\text{Cr}(\text{NO}_3)_3$ is obtained by dissolving the hydroxide in nitric acid and crystallises with $9\text{H}_2\text{O}$. It is stable in the violet form and its solution only very slowly becomes green on heating, recovering

the violet colour on cooling. The chloride and sulphate readily form green solutions on heating and these pass into the violet form only on long standing in the cold. If the acid formed by hydrolysis is nearly neutralised by alkali, and then an acid is added, a violet solution is rapidly formed.

Chromic phosphate CrPO_4 is formed as an amorphous violet precipitate from chromic salts and sodium phosphate solution. On standing for a day or two in contact with the solution it forms a violet crystalline hexahydrate $\text{CrPO}_4 \cdot 6\text{H}_2\text{O}$. On standing for a week a green amorphous tetrahydrate $\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$ is formed. A green crystalline tetrahydrate is formed by boiling the violet hexahydrate with water for half an hour, and a green dihydrate by boiling the other hydrates with acetic anhydride. All the hydrates give a black powder of CrPO_4 on heating.

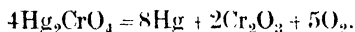
Chromic oxide (*chromium sesquioxide*) is formed as a green powder insoluble in water by heating chromic hydroxide or ammonium dichromate :



or heating sodium dichromate with sulphur in an iron pot and washing out the sodium sulphate from the residue :

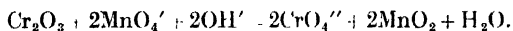


A very fine green oxide is produced by gently heating mercurous chromate :



Dark-green hard hexagonal crystals are formed by fusing the oxide with calcium carbonate and boron trioxide, by igniting a mixture of potassium dichromate and common salt, or by passing chromyl chloride vapour through a red-hot tube : $4\text{CrO}_2\text{Cl}_2 = 2\text{Cr}_2\text{O}_3 + \text{O}_2 + 4\text{Cl}_2$.

The crystalline oxide or that produced by ignition of the hydroxide or ammonium dichromate is insoluble in acids, except hot 70 per cent perchloric acid which oxidises it to CrO_3 ; it may be made soluble by fusing with potassium hydrogen sulphate (forming chromic sulphate) or sodium peroxide (forming sodium chromate), or by heating with alkaline permanganate when a chromate is formed and manganese dioxide precipitated



Chromic oxide has a very high melting point and is very refractory, but it dissolves in fused borax or glass, giving a green colour which becomes blue if strontium is present ; this is used in tinting glass and painting porcelain. The oxide is used as a permanent green oil paint called *chrome-green*. (It is often replaced by a mixture of Prussian blue and lead chromate, which is less permanent).

Chromic hydroxide is formed as a pale greyish-green flocculent precipitate by adding an alkali hydroxide or ammonia to a solution of a

chromic salt. According to Siewert (1861) pure chromic hydroxide is precipitated from *boiling* solutions of chromic salts by ammonia. From cold solution the precipitate contains ammonium salt, and if precipitated by potassium or sodium hydroxide, or if alkali salts are present in the solution, it contains alkali which is not removed by washing. The precipitate when dried over concentrated sulphuric acid has the composition $\text{Cr}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$. On standing in contact with dilute alkali the precipitate slowly "ages" and changes its properties.

A dark-green colloidal solution is obtained by dialysing a solution of the freshly-precipitated hydroxide in chromic chloride solution. It can be boiled but is precipitated by salts. Chromium hydroxide, like aluminium hydroxide, is appreciably soluble in *concentrated* ammonia, and in presence of large amounts of ammonium salts pink solutions containing **chromamines**, e.g. $[\text{CrCl}(\text{NH}_3)_4\text{H}_2\text{O}]\text{Cl}_2$ are formed.

By fusing together equimolecular amounts of potassium dichromate and crystallised boric acid and lixiviating with water, a brilliant-green powder is left, used as a pigment under the name of *Guignet's green*. This is usually supposed to be the hydroxide $\text{Cr}_2\text{O}(\text{OH})_4$ but usually contains some boric acid; a product $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ free from boric acid was obtained by Simon (1929).

Precipitated chromic hydroxide dissolves in sodium or potassium hydroxide solution to form a grass-green solution which may contain a **chromite**. All the chromic hydroxide is precipitated from the solution on boiling, and it has been supposed to be present as a colloidal solution. Solid crystalline alkali chromites are $\text{K}_3\text{CrO}_3 \cdot 4\text{H}_2\text{O}$, $\text{Na}_3\text{CrO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Na}_5\text{CrO}_4 \cdot 8\text{H}_2\text{O}$ (Fricke and Windhausen, 1924; Scholder and Pättsch, 1934). Chrome-ironstone has been regarded as ferrous chromite $\text{Fe}(\text{CrO}_2)_2$.

Chromic sulphide Cr_2S_3 is obtained in dark-green or black crystals by heating sulphur with chromium, or CrCl_3 in H_2S . It is not decomposed by water or acids, but on adding a solution of ammonium sulphide to a chromic salt only chromic hydroxide is precipitated:



Chromic sulphate is obtained as a bluish-violet crystalline mass by allowing a mixture of equal parts of concentrated sulphuric acid and chromic hydroxide (dried at 100°) to stand for some weeks in a loosely-stoppered bottle. From its solution in water containing a little alcohol violet octahedra of $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ are deposited.

By heating potassium dichromate or chrome alum with concentrated sulphuric acid an olive-coloured acid sulphate $2\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ completely insoluble in water and acids is formed.

Chromic sulphate forms alums with alkali metal sulphates. **Potassium chromic sulphate** or ordinary *chrome alum* $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ or

$\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$ is obtained by reducing a solution of potassium dichromate acidified with sulphuric acid, and forms dark-purple octahedral crystals. These are also formed on the carbon plate in dichromate cells after use. Chrome alum is formed as a by-product in the oxidation of anthracene to anthraquinone by sulphuric acid and potassium dichromate. It is used in dyeing and calico-printing and in tanning. The following experiment is a convenient method of preparation :

Dissolve 20 gm. of potassium dichromate in 150 ml. of hot water and after cooling add 4 ml. of concentrated sulphuric acid. Pass sulphur dioxide slowly into the *well-cooled* solution until the red colour, which at first changes to brown and then to olive-green, becomes greenish-blue :



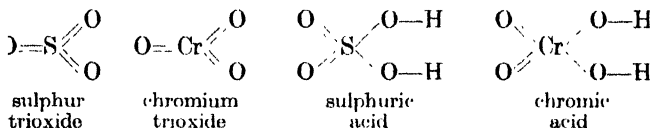
Set aside in a covered dish for some time and observe the formation of purple octahedral crystals of chrome alum. Instead of sulphur dioxide, alcohol may be used in the reduction and is oxidised to aldehyde.

A solution of chrome alum in cold water is dull bluish-red ; on heating to 70° it becomes green. Barium chloride precipitates the violet solution completely whilst the green solution is not completely precipitated. If the green solution is allowed to stand for some time in the cold it becomes violet.

Chromic acetate is obtained as a green solution, used as a mordant, by dissolving the hydroxide in acetic acid. **Chromicyanides**, *e.g.* $\text{K}_3\text{Cr}(\text{CN})_6$ and $\text{Ag}_3\text{Cr}(\text{CN})_6$, analogous to ferricyanides, and **chromithiocyanates**, *e.g.* $\text{K}_3\text{Cr}(\text{CNS})_6, 4\text{H}_2\text{O}$ (dark red), are stable and crystalline.

CHROMIUM TRIOXIDE AND THE CHROMATES

The acidic chromium trioxide CrO_3 contains 6-valent chromium and forms salts derived from a chromic acid H_2CrO_4 which is not known but is analogous to sulphuric acid :

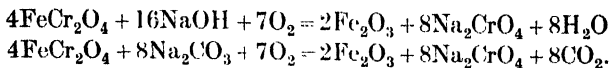


Chromic acid forms normal **chromates** (*e.g.* K_2CrO_4) and **dichromates** (*e.g.* $\text{K}_2\text{Cr}_2\text{O}_7$), analogous to sulphates and disulphates.* Acid chromates, *e.g.* KHCrO_4 are not known, but by the action of excess of CrO_3 or by boiling the dichromate with nitric acid, **trichromates** (*e.g.* $\text{K}_2\text{Cr}_3\text{O}_{10}$ or $\text{K}_2\text{O}, 3\text{CrO}_3$) and **tetrachromates** (*e.g.* $\text{K}_2\text{Cr}_4\text{O}_{13}$ or $\text{K}_2\text{O}, 4\text{CrO}_3$) are formed as red crystals.

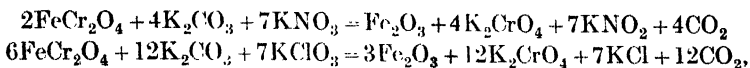
* A common mistake is to suppose that a dichromate is formed by "oxidising" a chromate (as a permanganate is formed by oxidising a manganate). Both chromate and dichromate contain the same 6-valent chromium.

In the manufacture of chromates and dichromates the starting material is the mineral *chromite* or *chrome ironstone* FeCr_2O_4 (ferrous chromite).

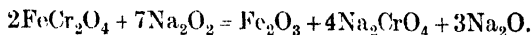
When finely-powdered chromite is strongly heated with an alkali or alkali carbonate with free exposure to air, the chromium is slowly oxidised to a soluble chromate and the ferrous iron to ferric oxide :



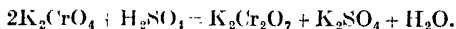
Oxidation is faster with a mixture of alkali carbonate and potassium nitrate or chlorate :



or with sodium peroxide :



On the technical scale fusion with potassium carbonate was formerly used, the yellow solution of potassium chromate being acidified with sulphuric acid, when on cooling potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ is formed in bright-red crystals :



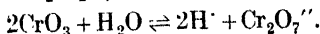
In the modern process a mixture of finely-powdered chromite, sodium carbonate and quicklime is heated to redness on the hearth of a reverberatory furnace with free exposure to air, when carbon dioxide is evolved and sodium chromate is formed. The function of the quicklime is probably to keep the mass porous and prevent fusion. The sodium chromate is extracted with water and concentrated sulphuric acid is added :



The sodium sulphate crystallises and is removed. The solution is concentrated and deliquescent red crystals of sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ slowly separate on cooling.

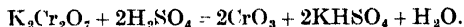
Sodium dichromate is cheaper and more soluble, but may be converted into potassium dichromate by crystallising from a solution of sodium dichromate and potassium chloride. Chromates and dichromates are used as oxidising agents, as mordants in dyeing, and in preparing insoluble pigments.

By the action of concentrated sulphuric acid on a solution of a chromate or dichromate, red chromium trioxide CrO_3 is obtained. This is often called "chromic acid" although it is the anhydride of this acid, which would have the formula H_2CrO_4 . The solution of chromium trioxide is red in colour and strongly acid. The colour, the depression of freezing point, and the conductivity show that the substance present is mostly dichromic acid $\text{H}_2\text{Cr}_2\text{O}_7$ or the ion $\text{Cr}_2\text{O}_7''$:



Chromium trioxide is prepared in the laboratory as follows :

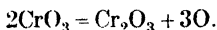
Dissolve 50 gm. of $K_2Cr_2O_7$ in 85 ml. of hot water and to the cooled solution add slowly with stirring 70 ml. of concentrated H_2SO_4 . Allow to stand for twelve hours and pour the liquid off the crystals of potassium hydrogen sulphate which have separated :



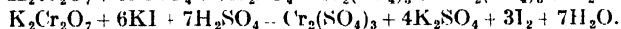
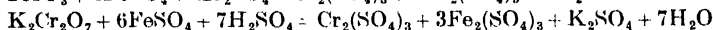
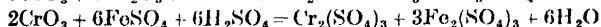
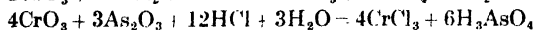
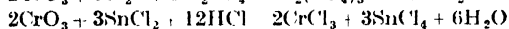
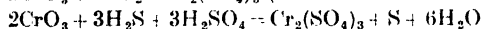
Heat to 85° , add 25 ml. of sulphuric acid and just sufficient water to dissolve the CrO_3 separating. Allow to stand twelve hours and decant the liquid from the crystals of CrO_3 . Wash the latter with pure nitric acid in a Buchner funnel containing asbestos, drain well and heat to 60° to 80° in a tube in a current of pure dry air to remove adhering nitric acid.

Pure chromium trioxide forms small bright violet-red needle-shaped crystals ; the commercial substance is a red solid. Chromium trioxide is very deliquescent. It melts at 198° to a dark-red liquid, solidifying on cooling to a reddish-black mass with a metallic lustre. When heated at 420° it loses oxygen : $4CrO_3 = 2Cr_2O_3 + 3O_2$, and a little of the trioxide sublimes. Chromium dioxide CrO_2 is said to be formed as an intermediate stage, or by heating chromic nitrate, but it has a somewhat variable composition. It may be formulated as basic chromium chromate $(Cr^{III}O)_2Cr^{VI}O_4$.

Chromium trioxide is a very powerful oxidising agent. Alcohol dropped on it inflames and the concentrated solution is reduced by sugar, oxalic acid, paper, cork, etc. It oxidises sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, iodides, etc. In acid solutions the reduction is always to a chromic salt :



$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3$ (some dithionate is also formed)



A solution of potassium dichromate mixed with sulphuric acid is very often used as an oxidising agent ; a solution of chromium trioxide in glacial acetic acid (which is not oxidised) is also used.

Chromates. – Metallic chromates if soluble are formed from the oxides, hydroxides, or carbonates and chromium trioxide ; if insoluble they can be prepared by double decomposition. All soluble chromates are poisonous.

Potassium chromate K_2CrO_4 is obtained in lemon-yellow readily soluble crystals, m. pt. 968.3° , by evaporating a solution prepared by adding the correct amount of potassium hydroxide or carbonate to a solu-

tion of chromium trioxide or potassium dichromate. The salt is isomorphous with potassium sulphate. Its yellow solution is alkaline.

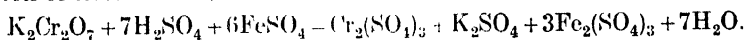
Potassium dichromate $K_2Cr_2O_7$ may be obtained by adding the requisite amount of sulphuric acid to a saturated solution of the normal chromate, and crystallises on cooling in garnet-red crystals, m. pt. 396° . It is much less soluble than the normal chromate and forms an orange-red solution with an acid reaction.

Both potassium salts are non-deliquescent and crystallise without water. The solubilities of the two salts in 100 parts of water are :

	0°	30°	60°	105.6°	104.8°
K_2CrO_4 - -	57.11	65.13	74.60	88.8 (b.pt.)	—
$K_2Cr_2O_7$ - -	4.64	18.09	16.10	—	106.2 (b.pt.)

Sodium chromate $Na_2CrO_4 \cdot 10H_2O$ and **dichromate** $Na_2Cr_2O_7 \cdot 2H_2O$, made on a large scale, are deliquescent. **Ammonium chromate** $(NH_4)_2CrO_4$ is unstable and tends to lose ammonia, forming the dichromate; it is obtained by crystallising from solutions containing excess of ammonia. **Ammonium dichromate** $(NH_4)_2Cr_2O_7$ is readily obtained by adding ammonia to the requisite amount of chromium trioxide in solution and crystallising. It forms orange-red crystals which decompose violently on heating, evolving nitrogen and steam and leaving a voluminous dull-green mass of chromic oxide: $(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$.

Potassium dichromate is used in volumetric analysis for the estimation of ferrous iron :



The most important sparingly soluble chromates are :

Silver chromate Ag_2CrO_4 , brick-red, rather sparingly soluble in acids and ammonia.

Barium chromate $BaCrO_4$, yellow, insoluble in acetic acid, soluble in hydrochloric, nitric and chromic acids; used in the gravimetric determination of barium or a chromate.

Zinc chromate (basic) $Zn_2(OH)_2CrO_4 \cdot H_2O$, a yellow pigment.

Lead chromate $PbCrO_4$ (*chrome-yellow*)—used as a pigment), precipitated from $Pb(NO_3)_2$ and $K_2Cr_2O_7$, soluble in nitric acid and in alkali hydroxide (forming a chromate and a plumbite), the least soluble lead salt but more soluble in hot water.

Basic lead chromate Pb_2CrO_5 (*chrome-red*)—used as a pigment), formed by digesting $PbCrO_4$ with cold sodium hydroxide solution; mixed with $PbCrO_4$ it forms the pigment *chrome-orange*.

Basic bismuth dichromate $(BiO)_2Cr_2O_7$, orange yellow.

Chromyl chloride.—Sulphuryl chloride SO_2Cl_2 is the chloride of sulphuric acid $SO_2(OH)_2$, and chromyl chloride CrO_2Cl_2 is the chloride of the hypothetical chromic acid $CrO_2(OH)_2$ or H_2CrO_4 :

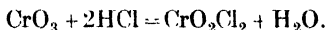


Chromyl chloride is prepared by distilling a dry mixture of sodium chloride and potassium dichromate with concentrated sulphuric acid in a retort; a deep-red vapour of chromyl chloride condenses in a cooled receiver to a deep-red (nearly black) liquid like bromine:

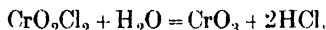


Bromides and iodides do not produce corresponding compounds when distilled with dichromate and sulphuric acid but the free halogen is liberated: this may be used in the detection of chlorides in presence of bromides and iodides, since if a chloride is present the distillate when collected in water produces chromic acid and gives with lead salts a yellow precipitate of PbCrO_4 .

If concentrated sulphuric acid is added in small quantities at a time to a cooled solution of chromium trioxide in concentrated hydrochloric acid, chromyl chloride separates:

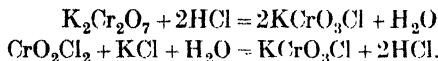


Chromyl chloride, b. pt. 116.7° , has the normal vapour density. It is violently decomposed by water:

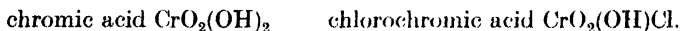


Chromyl chloride is a powerful oxidising agent, exploding in contact with phosphorus (*cf.* Br_2) and inflaming sulphur, ammonia, alcohol and many organic substances.

When three parts of powdered potassium dichromate are dissolved in four parts of warm concentrated hydrochloric acid and a little water and the liquid cooled, or if chromyl chloride is added to saturated potassium chloride solution, red crystals of potassium chlorochromate KCrO_3Cl (*Peligo's salt*) are formed:



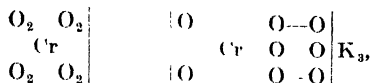
This may be regarded as derived from a *hypothetical* chlorochromic acid:



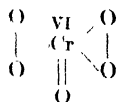
Perchromic acid.—If a solution of chromic acid or of a chromate acidified with sulphuric acid is added to hydrogen peroxide solution, a blue liquid is produced which gives a deep indigo-blue colour in ether when shaken with it. This blue solution contains a higher oxygen compound of chromium called perchromic acid. On standing over dilute *acid*, the solution in ether slowly loses its colour and the dilute acid becomes green from formation of a chromic salt. On addition of *alkali* to the blue ether solution, oxygen is evolved and a chromate is formed.

By the action of organic bases (aniline, pyridine, etc.) on the blue ether solution, *deep-blue* salts are formed which are explosive. These have been represented as $\text{CrO}_4(\text{OR})_2\text{H}_2\text{O}_2$, derived from HCrO_5 , or as acids salts RH_2CrO_7 , derived from H_3CrO_7 , but they appear to be addition compounds

of an oxide CrO_5 and not true salts. When ammonia gas is passed into the blue solution in ether the compound $\text{CrO}_4 \cdot 3\text{NH}_3$ separates. From alkaline chromate solutions and H_2O_2 , red salts of the formula $\text{K}_3(\text{CrO}_8)$ are obtained, which on treatment with acids evolve oxygen and form the blue salts. The red salt $\text{K}_3(\text{CrO}_8)$ appears to be:



containing 5-valent chromium and having an odd electron, as confirmed by its paramagnetism. The blue perchromic acid was formulated as $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$ by Moissan and as $\text{H}_3(\text{CrO}_8)$ by Riesenfeld. Riesenfeld obtained very explosive dark-blue crystals by adding 97 per cent hydrogen peroxide to CrO_3 in methyl ether at -30° , pouring off the blue liquid from excess of CrO_3 and evaporating in a vacuum at -30° . He regarded it as free perchromic acid, $\text{H}_3(\text{CrO}_8) \cdot 2\text{H}_2\text{O}$, but according to Schwarz (1936) it is a compound of methyl ether with a non-acidic oxide of 6-valent chromium, CrO_5 , viz. $\text{CrO}_5 \cdot (\text{CH}_3)_2\text{O}$, the oxide being:



The atomic weight of chromium has been found by reducing silver chromate and dichromate with sulphurous acid and precipitating the silver as chloride or bromide. The valency is found from the atomic heat, the vapour density of CrCl_3 and CrO_2Cl_2 , and the isomorphism of chromates and sulphates.

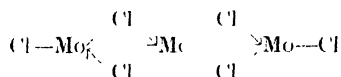
MOLYBDENUM

The mineral *molybdenite*, which is found in Norway, Mexico, Colorado, Korea, and China, resembles graphite but was found by Scheele (1778) to consist of molybdenum sulphide MoS_2 . When roasted in air it leaves a residue of molybdenum trioxide MoO_3 which dissolves in excess of ammonia to form ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$. The crystals obtained by evaporation (ordinary "ammonium molybdate") are more complex, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{21} \cdot 4\text{H}_2\text{O}$. Molybdenum and tungsten show marked tendencies to form such complex compounds. A solution of ammonium molybdate in nitric acid gives with phosphoric acid in the cold a canary-yellow precipitate of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$, which when heated for some time at 150° - 180° leaves ammonium phosphomolybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. On gentle ignition a black residue of $\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3$ is left. A solution of ammonium molybdate in dilute nitric acid slowly deposits yellow α -molybdic acid $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ which at 70° in water forms white β -molybdic acid H_2MoO_4 . Colloidal molybdic acid is formed by dialysing a solution of ammonium molybdate and hydrochloric acid; it forms a gum on evaporation.

On heating molybdic acids or ammonium molybdate, white molybdenum dioxide MoO_3 , which sublimes on heating, is formed. On heating this in hydrogen at 500° it forms reddish-brown molybdenum dioxide MoO_2 , and

this is reduced in hydrogen at 1200° to a grey powder of **metallic molybdenum**. Molybdenum (discovered by Hjelm in 1782) is made commercially by strongly heating molybdenum trioxide with carbon. The grey powder sinters at 1000° and can be hammered into rods, which are drawn into fine wire, used to support tungsten filaments in electric lamps. The metal is silver-white, fairly soft, oxidises slowly in air at room temperature and rapidly on heating, and burns when heated in oxygen, forming volatile MoO_3 . *Ferromolybdenum* is used in making alloy steels.

Molybdenum shows valencies of 2, 3, 4, 5, and 6, the compounds with lower valencies being reducing agents. **Molybdenum hexafluoride** MoF_6 , the only fluoride known and the only halide of 6-valent molybdenum, is formed in colourless crystals by direct combination of the metal and fluorine. **Molybdenum pentachloride** MoCl_5 sublimes in black crystals on heating molybdenum in chlorine. It fumes in moist air. **Molybdenum tetrachloride** MoCl_4 is formed as a brown sublimate on heating molybdenum trichloride $\cdot 2\text{MoCl}_3 = \text{MoCl}_4 + \text{MoCl}_5$, the **trichloride** being formed in copper-red crystals by passing a mixture of MoCl_5 vapour and carbon dioxide through a heated tube. The trichloride is insoluble, but forms a soluble red hydrate $\text{MoCl}_3 \cdot 3\text{H}_2\text{O}$ (cf. CrCl_3), obtained in solution by electrolytic reduction of a solution of MoO_3 in hydrochloric acid. Compounds of divalent molybdenum are unimportant; the so-called **dichloride**, an amorphous yellow solid formed by heating MoCl_3 in dry carbon dioxide, is Mo_2Cl_6 and probably has the structure



and similar compounds are formed with other acid radicals.

Besides the well-known molybdenum trioxide, there is a **pentoxide** Mo_2O_7 , formed by heating Mo and MoO_3 at 750°, and **hydroxides** $\text{MoO}(\text{OH})_3$ and $\text{Mo}(\text{OH})_7$.

Molybdocyanides $\text{M}_3\text{Mo}(\text{CN})_8$ contain 5-valent molybdenum and **molybdocyanides** $\text{M}_4\text{Mo}(\text{CN})_8$ contain 4-valent molybdenum; the latter give a blue colour with ferric salts. In these compounds molybdenum has the coordination number 8.

An important compound is **phosphomolybdic acid**, usually formulated as $\text{P}_2\text{O}_5 \cdot 24\text{MoO}_3 \cdot 63\text{H}_2\text{O}$, obtained in deep-yellow crystals by heating ammonium phosphomolybdate with aqua regia and recrystallising from water containing a little nitric acid.

TUNGSTEN

The heavy mineral which is now called *scheelite* was found by Scheele in 1781 to be **calcium tungstate**, CaWO_4 . A commoner mineral is *wolfram*, **ferrous tungstate** FeWO_4 found with tinstone in Cornwall but most abundantly in Burma and China. If these minerals are boiled with concentrated hydrochloric acid, a yellow powder of **tungsten trioxide** WO_3 ("tungstic acid") remains.

Metallic tungsten is obtained by reducing the trioxide with carbon hydrogen at a red heat: **ferrotungsten**, obtained in the electric furnace used for special steels (7-20 per cent of W; 2-6 per cent of Cr.) Tungst-

filaments (m.pt. 3400°) are used in electric lamps. They are made by reducing pure tungsten trioxide in dry hydrogen at 1200° , pressing the tungsten powder into rods, sintering these at 2500° in hydrogen, rolling and hammering at a high temperature, and then drawing at 400° - 600° , finally through a bored diamond.

Tungsten burns to WO_3 in oxygen at a red heat and in chlorine to WCl_6 at 250° - 300° . It is only slowly attacked by acids but rapidly by fused alkali.

Tungsten shows valencies of 2, 3, 4, 5, and 6, the compounds with lower valencies being reducing agents. It shows a greater tendency than molybdenum to form complex compounds.

Tungsten hexafluoride WF_6 is a colourless fuming liquid, b. pt. 19.6° , formed by distilling the hexachloride with anhydrous hydrofluoric acid: $WCl_6 + 6HF = WF_6 + 6HCl$. **Tungsten hexachloride** WCl_6 is formed in black crystals, m. pt. 275° , by heating tungsten in dry air-free chlorine: it is insoluble in water. Two **oxychlorides** known are red $WOCl_4$ and yellow WO_2Cl_2 . **Tungsten pentachloride** WCl_5 , **tungsten tetrachloride** WCl_4 , and **tungsten dichloride** W_3Cl_8 (with the same structure as Mo_3Cl_8) are known, but tungsten trichloride is known only in the form of greenish-yellow double salts $M_2W_2Cl_6$.

If tungsten trioxide (or wolfram) is heated with sodium carbonate, soluble **sodium paratungstate**, a complex salt, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, is obtained, which is used as a mordant and in rendering flannelette non-inflammable. This is derived from a hypothetical paratungstic acid $H_{10}W_{12}O_{41}$ or $12WO_3 + 5H_2O$.

From a solution of sodium paratungstate in the cold, hydrochloric acid precipitates white α -**tungstic acid**, $H_2WO_4 \cdot H_2O$, appreciably soluble in water. From hot solutions, yellow insoluble β -**tungstic acid**, H_2WO_4 , is thrown down. **Colloidal tungstic acid** is obtained by dialysing a solution of sodium tungstate to which hydrochloric acid has been added. When a solution of sodium paratungstate is boiled with tungsten trioxide **sodium metatungstate** is formed and can be obtained in crystals $Na_2W_7O_{21} \cdot 10H_2O$. This gives no precipitate with acids, since metatungstic acid is soluble; it can be obtained in crystals $H_2W_7O_{21} \cdot 8H_2O$. Metatungstic acid $H_2W_7O_{21}$ may be formulated as $4WO_3 + H_2O$.

Phosphotungstic acid $P_2O_5 \cdot 24WO_3 \cdot 63H_2O$, obtained by acidifying a solution of sodium phosphate and sodium tungstate with sulphuric acid, is crystalline and is soluble in ether, and is used as a reagent for alkaloids and proteins, which it precipitates. It also precipitates potassium and ammonium (but not sodium) salts.

URANIUM

The black mineral called *pitchblende*, found in Cornwall, Bohemia, East Africa, the Caucasus, and especially in Canada (Great Bear Lake), was found by Klaproth (1789) to be the oxide of a metal which he called uranium; it is U_3O_8 . *Carnotite* is a vanadate of uranium and potassium (40 per cent of U). All these ores contain traces of radium. If pitchblende is dissolved in concentrated sulphuric acid, the lead etc. separated by H_2S , and ammonia added to the filtrate, a precipitate of ferric hydroxide

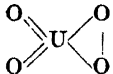
and **uranyl hydroxide** $\text{UO}_2(\text{OH})_2$, is formed. From this ammonium carbonate dissolves the uranium, forming a crystalline compound $\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$, which on ignition yields the pure oxide U_3O_8 . When this is dissolved in nitric acid, yellow fluorescent crystals of **uranyl nitrate** $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, commonly called "uranium nitrate," separate. Uranium salts mostly contain the bivalent uranyl radical UO_2 . They are used in photography and in making fluorescent glass.

Uranium shows valencies of 3, 4, 5 and 6. The chlorides UCl_5 , UCl_4 , and UCl_3 , and the fluorides UF_4 and UF_6 , are known. Uranium tetrachloride UCl_4 sublimes in green crystals on heating a mixture of UO_2 or U_3O_8 and carbon in a stream of chlorine; it is soluble in water, alcohol, and benzene. Uranium pentachloride UCl_5 (the only compound of 5-valent uranium) is a red or brown solid formed by the action of chlorine on UCl_4 . Uranium trichloride UCl_3 is formed in red needles by heating UCl_4 in hydrogen, or as a red solution by reducing a solution of UCl_4 in hydrochloric acid with zinc; it is a strong reducing agent. Uranium hexafluoride UF_6 (white, soluble solid) and uranium tetrafluoride UF_4 (green, insoluble solid) are formed by the reaction $2\text{UCl}_5 + 5\text{F}_2 = \text{UF}_6 + \text{UF}_4 + 5\text{Cl}_2$. Uranium oxyfluorides UOF_2 and UO_2F_2 are known. Uranium oxychloride UO_2Cl_2 (*cf.* CrO_2Cl_2) is formed by heating the oxide with charcoal in chlorine. It was thought to be uranium chloride until Peligot (1841) showed that, when heated with carbon in a current of chlorine, carbon monoxide is formed and dark-green crystals of UCl_4 sublime. By heating UCl_4 with sodium he obtained **metallic uranium**. Alloys with iron are obtained in the electric furnace, and used in making special steels.

Metallic uranium is difficult to obtain pure as it combines easily with oxygen, nitrogen and carbon. It is silver-white, malleable and ductile, density 18.7, giving strong sparks when filed and when the powder is thrown into a flame. The powder oxidises in air and slowly decomposes water. On heating it burns in oxygen to U_3O_8 and in chlorine to UCl_4 . It forms a hydride UH_3 , and a yellow nitride $\text{U}^{\text{IV}}_3\text{N}_4$ at 1000° .

The common oxide is U_3O_8 ; when strongly heated in hydrogen this forms the black dioxide UO_2 , dissolving in acids to form uranyl salts. The trioxide UO_3 is acidic and is formed by heating uranyl nitrate at 250° or the peroxide UO_4 in oxygen. It forms **uranic acids** H_2UO_4 , $\text{H}_2\text{UO}_4 \cdot \text{H}_2\text{O}$, and $\text{H}_2\text{U}_2\text{O}_7$. The **uranates** are precipitated by alkalis from uranyl salt solutions: $\text{UO}_2^{++} + 4\text{OH}' = \text{UO}_4^{--} + 2\text{H}_2\text{O}$. The alkali uranates are usually formulated as $\text{K}_2\text{U}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$, the sodium salt (*uranium yellow*) being used for painting porcelain and making yellow fluorescent uranium glass; these salts may have more complicated formulae.

A yellowish-white **uranium peroxide** $\text{UO}_4 \cdot 3\text{H}_2\text{O}$, or $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ when dried at 100° , is precipitated by hydrogen peroxide from a uranyl salt solution:

its structure may be . A red colour due to a **peruranate** is formed

with hydrogen peroxide and alkali.

The **transuranic elements** are mentioned on p. 407.

The formulae of **complex tungstates**.—The alkali paratungstates have been formulated as $5\text{M}_2\text{O} \cdot 12\text{WO}_3$ or $3\text{M}_2\text{O} \cdot 7\text{WO}_3$; the decision on the basis of analyses is difficult on account of the high atomic weight of

tungsten but the most accurate analyses agreed with the formula $5M_2O, 12WO_3$ used on p. 895. Since ammonium molybdate has been shown by X-ray analysis to be $(NH_4)_6Mo_7O_{24}$, i.e. $3(NH_4)_2O, 7MoO_3$ (p. 893), it is supposed by analogy that the paratungstate has a similar formula, $3Na_2O, 7WO_3$ or $Na_6W_7O_{24}$ instead of $5Na_2O, 12WO_3$ or $Na_{10}W_{12}O_{41}$. The formula $M_2O, 4WO_3$ or $M_2W_4O_{13}$ for the metatungstate (p. 895) was also based on accurate analyses, but since its X-ray structure is regarded as analogous to that of the phosphotungstate (p. 895), containing the ion $[PW_{12}O_{40}]^{8-}$, metatungstic acid has been formulated as $H_6[H_2W_{12}O_{40}]$, i.e. $24WO_3, 4H_2O$, instead of $H_2W_4O_{13}$ or $4WO_3, H_2O$. Phosphotungstic acid can still be formulated as $2H_3[PW_{12}O_{40}] - 3H_2O, P_2O_5, 24WO_3$.

Polonium. In the hydrogen sulphide precipitate from a solution of pitchblende, Mme Curie (1898) discovered a radioactive element accompanying bismuth which she called *polonium*. It is identical with radium-F (p. 402) and emits α -rays to form inactive radium-G (radio-lead). Marckwald (1902) showed that it is precipitated on a plate of bismuth; it is separated from tellurium by precipitating the latter with hydrazine, when polonium remains in solution. It can also be separated by dialysis, since it behaves as a colloid.

CHAPTER XLV

MANGANESE AND RHENIUM

GROUP VII comprises the Sub-group *b* containing the halogen elements and the artificial element astatine (At), and Sub-group *a* containing the natural elements manganese and rhenium and the artificial element technetium (Tc).

Sub-group (<i>a</i>) even series:	At. No.	Electron configuration	Density	At. Vol.	M. Pt.	B. Pt.
Mn	25	2·8·13·2	7·39	7·4	1260°	1900°
Tc	43	2·8·18·14·1	-	—	—	-
Re	75	2·8·18·32·13·2	21·2	8·7	3167°	—

Sub-group (<i>b</i>) odd series:	At. No.	Electron configuration	Density	M. Pt.	B. Pt.
F	9	2·2·5	1·108	- 217·8	- 187
Cl	17	2·8·2·5	1·557	- 101·6	- 34·6
Br	35	2·8·18·2·5	2·948	7·2	58·7
I	53	2·8·18·18·2·5	3·706	113·9	184·4
At	85	2·8·18·32·18·2·5			

(The densities of the halogens are of the liquids at the b. pt.)

The marked disparity in properties between members of the even and odd series beginning in Group V and increasing in Group VI has now reached an acute stage. The only way in which manganese and rhenium resemble the halogens is in the formation of volatile acidic heptoxides Mn_2O_7 and Re_2O_7 , analogous to Cl_2O_7 (the corresponding oxides of the other halogens are unknown). Mn_2O_7 is explosive like Cl_2O_7 , but Re_2O_7 is not. The perchlorates, *e.g.* $KClO_4$, and permanganates, *e.g.* $KMnO_4$, are isomorphous and both silver perchlorate and permanganate are sparingly soluble in water.

In its remaining compounds manganese as a transitional element shows close analogies with chromium and iron. The metals are similar in physical properties, and both manganese and chromium form basic sesquioxides M_2O_3 , dioxides MO_2 , and acidic trioxides MO_3 (MnO_3 known only in its salts, the manganates). Potassium chromate (yellow K_2CrO_4 and potassium manganate (green) K_2MnO_4 are isomorphous. Manganese resembles magnesium and zinc in forming a sparingly soluble $MnNH_4PO_4$, and it resembles iron in forming three oxides of the types MO , M_2O_3 , and M_3O_4 , the first two basic, although the oxides M_2O_3 are also weakly acidic. The manganous salts are more stable than the ferrous salts; they do not oxidise in air and the sur-

phate is more stable to heat. The ferric and chromic compounds, on the other hand, are more stable than the manganic; MnCl_3 very easily decomposes into MnCl_2 and chlorine, and manganic salts are powerful oxidising agents. A manganese alum $\text{KMn}^{\text{III}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ resembles ferric alum but is less stable. Manganic salts are easily hydrolysed since $\text{Mn}(\text{OH})_3$ is a weak base and is amphoteric.

MANGANESE

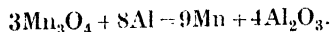
History.—The most important ore of manganese is the black dioxide MnO_2 , *pyrolusite*, referred to by Pliny as *magnes* but confused with the magnetic oxide of iron Fe_3O_4 . The name *pyrolusite* (Greek *pyr* fire, *luo* I wash) refers to the use of the mineral in decolorising green glass. If pyrolusite is added in small quantity the green ferrous silicate is oxidised to ferric silicate which has a pale-yellow colour, neutralised by the purple tinge due to the manganese. With excess of pyrolusite a violet colour is produced.

Pott in 1740 and Scheele in 1774 investigated pyrolusite. Metallic manganese was first obtained in an impure form by Gahn in 1774 by strongly heating the oxide with carbon. A purer metal was obtained by John in 1807.

Occurrence.—Pyrolusite occurs mainly in India, South Africa, the Gold Coast, and Russia. It is usually contaminated with ferric oxide and barium, often in the form of *psilomelane*, $(\text{Mn}, \text{Ba})\text{O} \cdot 2\text{MnO}_2$, corresponding with Weldon mud $\text{CaO} \cdot 2\text{MnO}_2$. Pyrolusite always contains less oxygen than corresponds with the formula MnO_2 . Most of the ore is now used in smelting for ferromanganese.

Less important minerals are *braunite* Mn_2O_3 , *hausmannite* Mn_3O_4 , *manganite* $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$, hydrated dioxides *wad* and *psilomelane*, *diopside* or *rhodocrosite* MnCO_3 , *rhodante* MnSiO_3 , *alabandite* MnS and *hauerite* MnS_2 . The deposits of hydrated oxides are sedimentary (precipitates, or derived from oxidation by plants etc. in lakes) or metamorphic (derived from the weathering of rocks). Manganese compounds in the soil are important in biological processes.

Metallic manganese.—Impure manganese is obtained by reducing the oxide Mn_3O_4 with carbon at a high temperature: $\text{Mn}_3\text{O}_4 + 4\text{C} = 3\text{Mn} + 4\text{CO}$. If less than the theoretical amount of carbon is used in the electric furnace, a purer metal (nearly free from carbon) is produced. A purer metal is obtained by heating the chloride with sodium or magnesium, or by reducing the oxide Mn_3O_4 with aluminium in the aluminothermic process (p. 882):



The purest metal is obtained by electrolysis of concentrated manganous chloride solution with a mercury cathode and distilling off the mercury in a vacuum at 250° .

Manganese is greyish-white, or reddish-white, hard and brittle, with a fairly high melting point, 1260°. When pure it is not easily oxidised by air. The metal unless very pure decomposes water even in the cold with evolution of hydrogen, and readily dissolves in dilute acids forming manganous salts and evolving hydrogen (even with cold dilute nitric acid): $\text{Mn} + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + \text{H}_2$. It unites directly with nitrogen at a high temperature forming nitrides Mn_3N_2 and Mn_5N_2 (also formed by passing ammonia over the heated metal), and with carbon in the electric furnace forming a soft carbide Mn_3C .

Alloys of iron and manganese are *ferromanganese* (70–80 per cent Mn and less than 0.3 per cent carbon) and *spiegeleisen* (so-called from its flat mirror-like crystals; 20–32 per cent Mn and more than 0.3 per cent carbon). *manganese steel* is very hard and tough and is used for jaws of rock-crushers and for machinery. *Manganese bronze* is copper alloyed with manganese and zinc. *Manganin* is an alloy of copper, manganese and nickel used for resistance coils. Pure manganese becomes appreciably magnetic only on heating; at room temperature it is paramagnetic. Some alloys (*Heusler's alloys*) of copper, aluminium and manganese are ferromagnetic.

Manganese forms series of compounds in which it has the valencies 1, 2, 3, 4, 6, and 7:

1. *Univalent manganese* is present in white $\text{Na}_3[\text{Mn}^{\text{I}}(\text{CN})_6]$, deposited when the deep-yellow solution of alkaline $\text{Na}_4\text{Mn}(\text{CN})_6$ reduced with aluminium is filtered into sodium cyanide solution saturated with sodium acetate.

2. Compounds of 2-valent manganese are the basic *monoxide* MnO and the common *manganous salts*, e.g. MnCl_2 and MnSO_4 .

3. Compounds of 3-valent manganese are the weakly acidic *sesquioxide* Mn_2O_3 , forming *manganites* $\text{M}^{\text{I}}(\text{Mn}^{\text{III}}\text{O}_2)$, and the *manganic compounds*, e.g. MnCl_3 and $\text{Mn}_2(\text{SO}_4)_3$.

4. Compounds of 4-valent manganese are the *dioxide* MnO_2 , acidic and forming *permanganites* $\text{M}_2^{\text{I}}(\text{Mn}^{\text{IV}}\text{O}_3)$, and compounds such as $\text{Mn}(\text{SO}_4)_2$.

6. Compounds of 6-valent manganese are the *manganates* $\text{M}_2^{\text{I}}\text{Mn}^{\text{VI}}\text{O}_7$, isomorphous with sulphates.

7. Compounds of 7-valent manganese are the *heptoxide* Mn_2O_7 , acidic and forming *permanganates* $\text{M}^{\text{I}}\text{Mn}^{\text{VII}}\text{O}_4$, isomorphous with perchlorates.

The electronic structure of the manganese atom is $2|2\cdot2\cdot4|2\cdot2\cdot4\cdot5|2$, total 25, the third quantum group containing 13 electrons. The loss of the two 4-quantum electrons gives the Mn^{++} ion. The other ions of different valency, including anions (manganate and permanganate ions) are formed by the 3-quantum electrons functioning as valency electrons:

Mn^+	$2 2\cdot2\cdot4 2\cdot2\cdot4\cdot5 1$	total 24	valency 1
Mn^{++}	$2 2\cdot2\cdot4 2\cdot2\cdot4\cdot5 $.. 23	.. 2
Mn^{+++}	$2 2\cdot2\cdot4 2\cdot2\cdot4\cdot4 $.. 22	.. 3
MnO_4^{--}	$2 2\cdot2\cdot4 2\cdot2\cdot4\cdot1 6(2)$.. 27	.. 6
MnO_4^-	$2 2\cdot2\cdot4 2\cdot2\cdot4 7(1)$.. 26	.. 7

The numbers in brackets () denote the electrons gained from hydrogen or metal atoms, which became cations. Some of the oxygens were assumed to be attached by coordinate links :



but the Mn to O distance in the tetrahedral MnO_4' ion of KMnO_4 corresponds with considerable double bond character, as it is similar to the distance in SO_4'' and ClO_4' .

MANGANOUS SALTS

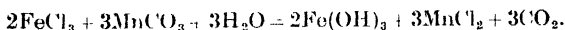
The soluble manganous salts MnX_2 are white or pale-pink and give pink solutions containing the *manganous ion*, probably hydrated, $[\text{Mn}(\text{H}_2\text{O})_4]^{++}$, also present in the crystal hydrates, which (unlike chromous and ferrous ions) shows practically no tendency to oxidise to higher valency. The hydroxide $\text{Mn}(\text{OH})_2$ is easily oxidised by atmospheric oxygen to manganic hydroxide : $4\text{Mn}(\text{OH})_2 + \text{O}_2 = 4\text{MnO}(\text{OH}) + 2\text{H}_2\text{O}$.

Manganous salts are formed by dissolving the metal or manganous carbonate in acids, but are usually prepared from manganese dioxide.

Manganous chloride is contained in the residues after the preparation of chlorine (p. 201) :



Since pyrolusite always contains iron the solution is yellow and contains ferric chloride FeCl_3 ; this prevents the crystallisation of the manganous chloride. In order to separate the iron, one-tenth of the filtered solution is evaporated to drive off excess of acid and is precipitated with sodium carbonate. Ferric hydroxide and manganous carbonate are thrown down. The precipitate is washed and added to the remainder of the solution. On boiling, the whole of the iron is precipitated as ferric hydroxide, manganese going into solution as chloride, and the filtered solution on evaporation deposits pink crystals of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$:



A hydrate $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$ is formed at -2° ; at 60° the ordinary form of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ passes into a second monoclinic form. At $58\cdot098^\circ$ $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ is obtained, which at 198° gives rose-red anhydrous MnCl_2 . This melts at 650° and volatilises at a higher temperature; the vapour density is normal. MnCl_2 forms a green solution in ether. It gives a green flame coloration. It combines with 1, 2 and 6 molecules of ammonia.

Manganous fluoride MnF_2 is a white powder, hydrolysed in solution, obtained by heating in CO_2 at 300° the white precipitate of $(\text{NH}_4)\text{MnF}_3$ thrown down by a large excess of ammonium fluoride solution from a solution of manganous chloride.

Manganous bromide $MnBr_2$ and $MnBr_2 \cdot 4H_2O$, and **manganous iodide** MnI_2 and $MnI_2 \cdot 4H_2O$, are similar to the chloride.

By heating the carbonate (or any higher oxide of manganese) in hydrogen, **manganous oxide** MnO is obtained as a greyish-green powder. If the hydrogen contains a trace of HCl emerald-green crystals of MnO are formed. Manganous oxide is also formed on heating the oxalate: $MnC_2O_4 = MnO + CO + CO_2$. If sodium or potassium hydroxide is added to a manganous salt solution white **manganous hydroxide** $Mn(OH)_2$ is precipitated, which in presence of air or oxygen rapidly oxidises to brown manganic hydroxide $MnO(OH)$.

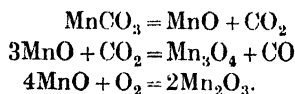
This reaction is used in determining oxygen dissolved in water; the precipitate is dissolved in hydrochloric acid, potassium iodide added, and the iodine titrated. One ml. of $N/10 I_2 = 0.0008$ gm. of O_2 .

Manganous hydroxide occurs native as *pyrochroite*, isomorphous with brucite $Mg(OH)_2$. Ammonia precipitates manganous hydroxide only slowly and the solution rapidly deposits $MnO(OH)$ on exposure to air. In presence of ammonium chloride only half the manganese is precipitated:



The usual method of precipitating the metals Fe, Al, Cr by $NH_4Cl + NH_4OH$, and then precipitating Mn in the filtrate with $(NH_4)HS$, is not applicable if manganese is present in large amounts.

Manganous carbonate $MnCO_3$ is formed as a white or pale buff-coloured precipitate on adding sodium bicarbonate to a solution of a manganous salt through which carbon dioxide is passed. (The precipitate contains manganous hydroxide if sodium carbonate is used.) It is sparingly soluble in water containing carbon dioxide to form a bicarbonate, and when moist readily oxidises in air to brown manganic hydroxide $MnO(OH)$ (*cf.* $FeCO_3$). It occurs as the bright-red mineral *rhodocrosite* or *manganese spar* isomorphous with calcite; the mineral *mangano-calcite* $(Mn, Ca, Mg)CO_3$ is isomorphous with aragonite. Manganese carbonate is decomposed by heat; at high temperatures or in presence of air a higher oxide of manganese is formed:



Manganous nitrate $Mn(NO_3)_2$ is obtained by dissolving manganous carbonate in a slight excess of dilute nitric acid or boiling manganese dioxide with dilute nitric acid containing oxalic acid or sugar. On evaporation pink deliquescent crystals $Mn(NO_3)_2 \cdot 6H_2O$, soluble in alcohol, are formed. On heating gently these decompose and deposit manganese dioxide (p. 905): $Mn(NO_3)_2 = MnO_2 + 2NO_2$, and anhydrous manganous nitrate is made by evaporating $Mn(NO_3)_2 \cdot 6H_2O$ with con-

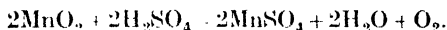
concentrated nitric acid to form $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, and then warming this with concentrated nitric acid containing N_2O_5 .

Manganous phosphate $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ is formed as a white amorphous precipitate on adding excess of sodium phosphate Na_2HPO_4 to a manganous salt solution.

Manganous ammonium phosphate $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ is formed as a reddish-white glittering crystalline precipitate by adding ammonium chloride, ammonia and sodium phosphate to a manganous salt solution. It can be dried and weighed as MnNH_4PO_4 in the determination of manganese. On heating to redness it forms the pyrophosphate $\text{Mn}_2\text{P}_2\text{O}_7$.

Manganous sulphide MnS occurs as the mineral *alabandite*. It is formed as a grey mass by heating the carbonate with sulphur, or the oxide, carbonate or sulphate in hydrogen sulphide; or as a light flesh-coloured powder by precipitating a manganous salt with ammonia and ammonium sulphide. In contact with excess of ammonium sulphide, or on heating in hydrogen sulphide at 320° , it passes into a green crystalline form. Manganous sulphide dissolves readily in dilute acids, even acetic; in this way manganese may be separated from zinc, the sulphide of which is insoluble in acetic acid.

Manganous sulphate MnSO_4 can be prepared from pyrolusite by heating with concentrated sulphuric acid:



The residue is heated to dull redness to decompose ferric sulphate: $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_3$, dissolved in water and the filtered solution evaporated, when pink crystals of the hydrated salt $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ separate. The last traces of iron may be removed by boiling the solution with a little precipitated manganous carbonate.

The solubility curve (Fig. 385) shows several hydrates: $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ (isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) below 9° ; between 9° and 27° $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (isomorphous with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$);

above 27° (when the solubility is a maximum) $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. The common crystalline salt $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ separates as a labile form in a

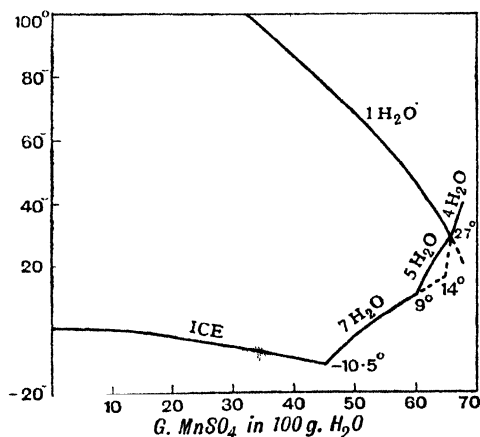


FIG. 385.—Manganous sulphate-water system.

restricted temperature interval about 26° , with a transition temperature at 14° between the 7 and $4\text{H}_2\text{O}$ forms. On heating at 280° almost white anhydrous MnSO_4 (m. pt. 700° , decomp. 850°) is formed. Well-crystallised double salts are $\text{K}_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (monoclinic, isomorphous with ferrous ammonium sulphate), and $\text{MnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, a pseudo-alum, is the mineral *apjohnite*.

Manganous borate $\text{MnH}_4(\text{BO}_3)_2$ is formed as an almost white powder by precipitating manganous sulphate or chloride solution with borax and drying at 100° . It is used as a *drier* for linseed oil, paints and varnishes: it acts catalytically, probably by the intermediate formation of a higher oxide. Manganous compounds give an amethyst-coloured borax bead.

MANGANIC COMPOUNDS

Except the oxide Mn_2O_3 the tervalent manganese compounds are much less stable than the bivalent. They are mostly covalent, and in solution either form complex ions (*e.g.* MnCl_6^{3-}) or tend to hydrolyse to a brown precipitate of manganic hydroxide $\text{MnO}(\text{OH})$, and are thus less stable than the chromic and ferric compounds they otherwise resemble.

Manganic fluoride MnF_3 is obtained as a purple solid by the action of fluorine on manganous iodide, and the hydrate $\text{MnF}_3 \cdot 3\text{H}_2\text{O}$ by dissolving Mn_2O_3 in hydrofluoric acid. Anhydrous MnF_3 decomposes on heating into manganous fluoride and fluorine: $2\text{MnF}_3 = 2\text{MnF}_2 + \text{F}_2$.

Manganic chloride or manganese trichloride MnCl_3 is probably contained in the dark-red or brown solution of manganese dioxide in cold concentrated hydrochloric acid: $2\text{MnO}_2 + 8\text{HCl} = 2\text{MnCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2$. On warming, chlorine is evolved: $2\text{MnCl}_3 = 2\text{MnCl}_2 + \text{Cl}_2$. A solid containing MnCl_3 is formed by passing hydrogen chloride into a suspension of manganese dioxide in carbon tetrachloride.

Pure MnCl_3 is obtained by the action of dry hydrogen chloride on manganic acetate (see below); it is stable below -35° but above this temperature it decomposes into manganous chloride and chlorine. A complex salt K_2MnCl_5 is formed by saturating the solution of manganese dioxide in hydrochloric acid with hydrogen chloride gas and adding solid potassium chloride.

Manganic oxide Mn_2O_3 occurs as *braunite* and hydrated $\text{MnO}(\text{OH})$ ($= \text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) as *manganite*. The oxide is formed as a black powder on heating MnO or MnO_2 to redness in air: $4\text{MnO} + \text{O}_2 = 2\text{Mn}_2\text{O}_3$. The hydrate $\text{MnO}(\text{OH})$ is formed as a dark-brown powder by passing chlorine into a suspension of manganous carbonate in water:



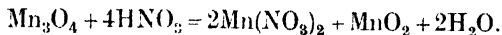
Excess of manganous carbonate is removed by very dilute nitric acid

Manganic oxide dissolves in dilute hydrofluoric or hydrocyanic acid and is a true manganic compound with the formula $O^{\cdot-}Mn-O-Mn=O$. When heated with nitric acid the oxide and hydrated oxide decompose into manganous nitrate and manganese dioxide :



Mangano-manganic oxide Mn_3O_4 (*red oxide of manganese*) occurs as *hausmannite*. It is formed as a brownish-red powder on strongly heating manganese dioxide out of contact with air or at 940° in air : $3MnO_2 = Mn_3O_4 + O_2$. It is probably manganous manganite MnO, Mn_2O_3 or $Mn^{II}(Mn^{III}O_2)_2$.

When boiled with dilute nitric acid it forms a solution of manganous nitrate and a black residue of manganese dioxide :



Manganic acetate $Mn(C_2H_3O_2)_3$ is obtained as a black solid by heating crystalline manganous nitrate $Mn(NO_3)_2 \cdot 2H_2O$ with acetic anhydride.

Manganic phosphate $MnPO_4 \cdot H_2O$ is formed as a greenish-grey precipitate by oxidising a boiling solution of manganous sulphate, acetic acid, and phosphoric acid with potassium permanganate.

Manganic sulphate $Mn_2(SO_4)_3$ is a dark-green powder obtained by heating precipitated manganese dioxide with concentrated sulphuric acid at 138° , draining on a porous plate, washing with concentrated nitric acid and heating at 130° to expel nitric acid :



It forms alums, the red caesium alum $CsMn(SO_4)_2 \cdot 12H_2O$ being most stable ; they tend to hydrolyse in solution. Manganic sulphate forms a violet solution which deposits $MnO(OH)$ on dilution.

QUADRIVALENT MANGANESE

The most familiar compound of Mn^{IV} is **manganese dioxide** $O^{\cdot-}Mn=O$. Manganese dioxide occurs native as *pyrolusite*. It is prepared in the pure state by heating about 600 gm. of manganous nitrate until red fumes appear, decanting the clear liquid from the residue of lower oxides and heating it for forty to sixty hours at 150° to 160° , when a hard lustrous black mass is formed : $Mn(NO_3)_2 - MnO_2 + 2NO_2$. The brown precipitates formed when solutions of manganous salts are treated with oxidising agents such as potassium permanganate, sodium hypochlorite, ammonia and bromine, or ozone, contain less oxygen than corresponds with the formula MnO_2 . Manganese dioxide is a feebly acidic oxide and with strong bases forms **permanganites** (often called *manganites*, which are properly compounds of Mn_2O_3) e.g. CaO, MnO_2 and $CaO, 2MnO_2$, although some are doubtful. A colloidal solution of

manganese dioxide is formed by the action of ammonia on boiling potassium permanganate solution.

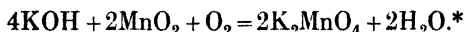
Besides its use in decolorising glass (p. 899), manganese dioxide is used (mixed with ferric oxide) as a dark-brown glaze on pottery, and as a depolariser in the Leclanché cell, when it is reduced to Mn_2O_3 .

Manganese tetrachloride $MnCl_4$ is not known but a complex salt K_2MnCl_6 is said to be formed by boiling potassium permanganate with glacial acetic acid and saturating the reddish-brown solution with hydrogen chloride.

Manganese disulphate $Mn(SO_4)_2$ is a powerful oxidising agent obtained as a brown solution by the electrolytic oxidation of manganous sulphate in fairly concentrated sulphuric acid. It is hydrolysed by water.

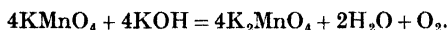
MANGANATES AND PERMANGANATES

On fusing manganese dioxide with sodium or potassium hydroxide in an iron dish with free access to air, a green mass is formed which contains a manganate, *e.g.* K_2MnO_4 . The reaction is more complete with potassium hydroxide and more rapid if potassium or sodium nitrate or chlorate is added :



The dark-green mass may be dissolved in a *small* quantity of cold water to form a dark-green solution, from which on evaporation in a vacuum dark-green crystals of the manganates K_2MnO_4 or $Na_2MnO_4 \cdot 10H_2O$ are deposited. These are isomorphous with the corresponding sulphates, K_2SO_4 and $Na_2SO_4 \cdot 10H_2O$. Sodium manganate is used as a disinfectant, since it is a powerful oxidising agent.

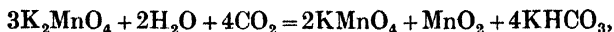
Potassium manganate is most easily prepared by boiling 10 gm. of potassium permanganate with a solution of 30 gm. of potassium hydroxide in 50 ml. of water to about half the volume, adding 25 ml. of water, cooling at 0° , and filtering the solid manganate on asbestos :



If the dark-green solution of the manganate is poured into a large volume of water a purple solution of permanganate and a brown precipitate of hydrated manganese dioxide are formed :

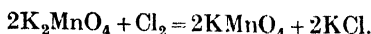


In presence of excess of alkali the reaction does not take place and the manganate is stable in alkaline solution. The reaction is complete if the alkali formed is removed by adding an acid, even carbonic acid by passing carbon dioxide into the solution :



* It should be noted that permanganate is *not* formed at this stage.

or the manganate may be converted into permanganate by passing chlorine into the solution :



Permanganate is also prepared by electrolytic anodic oxidation of the manganate solution :

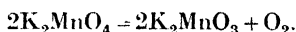


In the laboratory preparation of potassium permanganate a mixture of 50 gm. of powdered potassium hydroxide and 25 gm. of potassium chlorate is fused on one iron sand-bath covered with a second one. To the fused mass 50 gm. of finely-powdered pyrolusite are added gradually, stirring with an iron rod. The heating is continued until the mass stiffens : it is cooled and extracted with 1 litre of water. The liquid is boiled and carbon dioxide passed in until a drop of the liquid placed on filter paper gives a purple colour (no green). The liquid is allowed to settle, filtered through asbestos, evaporated to 300 ml. and filtered hot through asbestos. On cooling potassium permanganate crystallises. A further crop is obtained by evaporating the mother liquor to 100 ml.

Potassium permanganate forms deep purple-red brilliant rhombic prisms which have a green iridescence. It is rather sparingly soluble in water (5.31 in 100 at 15°, 32.4 at 75°) to a deep-purple solution which is opaque unless quite dilute. The crystals on heating evolve oxygen and fall to a black powder of potassium manganate and manganese dioxide :



At a red heat the manganate is decomposed into permanganite and oxygen :

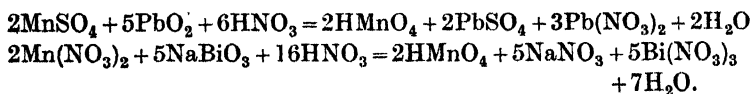


Mixtures of potassium permanganate with sulphur and charcoal deflagrate when kindled. The formula KMnO_4 (not $\text{K}_2\text{Mn}_2\text{O}_8$) is found from the basicity of permanganic acid as found by Ostwald's rule (p. 300). For potassium permanganate $\lambda_{32} = 121.7$ and $\lambda_{1024} = 132.4$, hence $B = 1$.

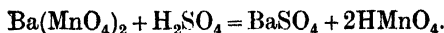
Barium permanganate is made by boiling a solution of potassium permanganate, barium nitrate, and barium hydroxide, washing the barium manganate BaMnO_4 precipitated with hot water, suspending it in water and passing in carbon dioxide and superheated steam for some hours ; the violet solution of barium permanganate formed is filtered from the barium carbonate through asbestos, evaporated and crystallised. Silver permanganate AgMnO_4 precipitates from mixed solutions of silver nitrate and potassium permanganate and may be crystallised from warm water.

Manganic acid is not known in the free state since manganates when acidified do not give manganic acid but permanganates. Permanganic acid HMnO_4 is formed in a deep-purple solution by boiling a solution of manganous sulphate or nitrate with lead dioxide and nitric acid, or

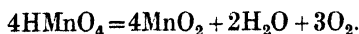
by oxidising a manganous salt solution with sodium bismuthate and nitric acid in the cold :



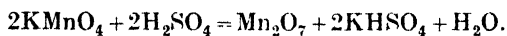
A pure solution is prepared by adding dilute sulphuric acid to a solution of barium permanganate :



Permanganic acid solution is a powerful oxidising agent ; it is unstable and decomposes with evolution of oxygen and deposition of manganese dioxide :



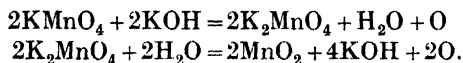
When powdered potassium permanganate is added in small quantities at a time to cooled concentrated sulphuric acid, a dark-green solution is formed *which is liable to explode violently* in contact with traces of organic matter or even spontaneously, *and should never be prepared in quantity*. When ice-cold water is cautiously added, dark-brown drops of manganese heptoxide Mn_2O_7 , the anhydride of permanganic acid, separate :



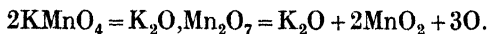
Manganese heptoxide, density 2.4, forms a violet vapour at 40° - 50° , but explodes violently on warming or in presence of organic matter. With water it forms a violet solution of permanganic acid.

Reactions of potassium permanganate.—Potassium permanganate is a powerful oxidising agent. The action is different in alkaline and acid solutions.

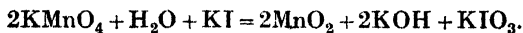
(1) In *alkaline solution* the permanganate is first reduced to green manganate. The solution then deposits brown manganese dioxide and becomes colourless :



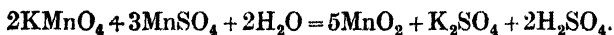
Hence two molecules of permanganate in *alkaline solution* give *three* atoms of available oxygen when reduced to manganese dioxide :



Alkaline permanganate oxidises iodides to iodates :



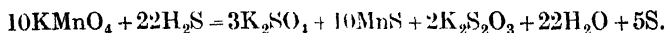
A manganous salt is oxidised in *neutral solution* in presence of zinc sulphate and zinc oxide to manganese dioxide (which may form zinc permanganite $\text{ZnO}, 2\text{MnO}_2$) :



Hydrogen sulphide reacts with *neutral* 1 per cent permanganate :

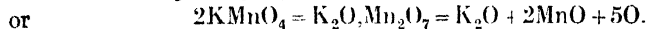
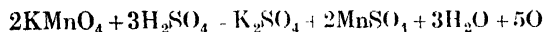


The reaction is really more complicated :

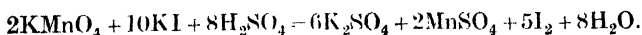


At the beginning of the reaction some dithionate $\text{K}_2\text{S}_2\text{O}_6$ is formed.

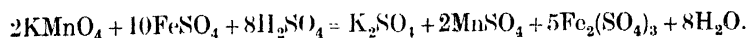
(2) In *acid solutions* two molecules of permanganate are reduced to a manganous salt and *five* atoms of oxygen become available :



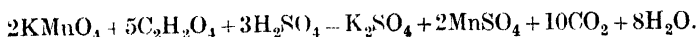
In *acid solutions* iodine is liberated from potassium iodide :



Ferrous salts are oxidised to ferric salts :



Oxalic acid is oxidised to carbon dioxide :

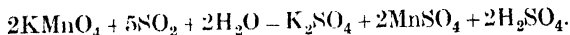


(This reaction is slow at first, unless some manganous sulphate is added, which acts as a catalyst).

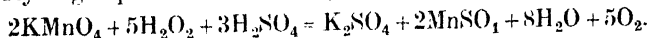
Nitrites are oxidised to nitrates :



Sulphur dioxide is oxidised to sulphuric acid :

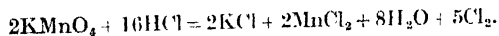


Hydrogen peroxide evolves oxygen :



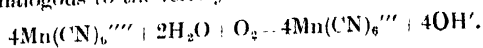
The reactions are accelerated by the presence of manganous salts, which act catalytically.

In presence of free hydrochloric acid, chlorine may be evolved from permanganate solution :



This may be prevented to some extent by adding a few grams of manganous sulphate and titrating in the cold. The manganous salt greatly increases the velocity of the primary reaction (*e.g.* oxidation of ferrous salt), but not that of the oxidation of hydrochloric acid.

Cyanogen compounds.—Potassium cyanide gives with solutions of manganous salts a yellowish-grey precipitate, sometimes said to be **manganous cyanide** $\text{Mn}(\text{CN})_2$, soluble in excess of the reagent to a yellow solution of potassium **manganocyanide** analogous to the ferrocyanide, which crystallises as a deep-blue solid $\text{K}_4\text{Mn}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. By evaporating this solution in air the manganese is oxidised and the solution contains **potassium manganicyanide** $\text{K}_3\text{Mn}(\text{CN})_6$ analogous to the ferricyanide :



This forms large red prisms. The resemblance between manganese and iron is apparent and the corresponding salts are isomorphous.

The atomic weight of manganese was determined from the ratios $\text{MnCl}_2 : 2\text{AgCl}$ and $\text{MnBr}_2 : 2\text{AgBr}$. The valency follows from the atomic heat and from the isomorphism of manganous and ferrous compounds.

RHENIUM

Rhenium, which was first identified by the X-ray spectrum (Noddack, Tacke and Berg, 1925), occurs in minerals of elements of adjoining groups, e.g. in columbite (a tantalum mineral) and in platinum ores, but only in very small quantities. It is not found in manganese ores. The chief occurrence of rhenium is in some molybdenites (MoS_2), which may contain as much as 2×10^{-6} gm. of Re per gm. The commercial rhenium is prepared from Mansfeld copper residues, being finally purified by precipitation as nitron perrhenate.

Rhenium forms four oxides, Re_2O_7 , ReO_3 , ReO_2 and Re_2O_3 . The most characteristic is the stable heptoxide, a pale-yellow crystalline solid formed by burning rhenium in oxygen. It begins to sublime at 220° , m.pt. 301.5° , b.pt. 363° . By subliming Re_2O_7 over heated rhenium the purplish-red solid trioxide ReO_3 , decomposing at 300° , is obtained. The black non-volatile dioxide is obtained by reduction of the higher oxides, or in a black hydrated form by reducing an acidified perrhenate solution. Hydrated Re_2O_3 is formed by the action of alkali on the trichloride; it liberates hydrogen from water.

Metallic rhenium, which resembles tungsten or osmium powder but is white like platinum in compact form, is easily obtained by heating potassium perrhenate, the oxides or sulphides, in hydrogen: m. pt. 3167° , density 21.2; it oxidises only at high temperatures and is substantially unaffected by acids, except nitric which converts it into perrhenic acid HReO_4 . Its electrical resistance is about four times that of tungsten. The atomic weight is 186.31, and there are two isotopes, 185 and 187, with an abundance ratio of 1.62 : 1.

Rhenium hexafluoride, ReF_6 , m. pt. 25.6° , b. pt. 47.6° , is formed from the elements; it is easily reduced by hydrogen to **rhenium tetrafluoride** ReF_4 , m. pt. 124.5° . **Oxyfluorides** are ReOF_4 , m. pt. 39.7° , and ReO_2F_2 , m. pt. 156° . **Rhenium pentachloride** ReCl_5 , obtained from the elements, is a black crystalline substance, volatile on heating in chlorine. It is hydrolysed by water, giving blue hydrated ReO_2 , but dissolves in a little water yielding a blue solution. On heating in nitrogen it forms **rhenium trichloride** ReCl_3 , and a **tribromide** ReBr_3 is known. By interaction of ReCl_5 and Re_2O_7 , **oxychlorides** are formed: ReOCl_4 , a brown crystalline solid, m. pt. 28° , and ReO_3Cl , a yellow liquid, m. pt. 4.5° , b. pt. 131° .

Rhenium heptoxide is remarkably soluble in water, forming **perrhenic acid** (up to 65 per cent by weight of HReO_4), which can only be reduced with difficulty. The solution is strongly acid, attacking most metals and dissolving the carbonates easily. The perrhenates are very characteristic and stable. The ion is colourless. KReO_4 (which can be melted without decomposition) is much less soluble than NaReO_4 (as with the permanganates). On reduction, perrhenate solutions exhibit a series of colour

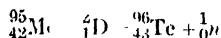
changes corresponding with lower valency states, perhaps as low as bivalent, but the compounds have not been isolated.

A green **barium rhenate** BaReO_4 corresponds with an unknown rhenic acid H_2ReO_4 ; brown alkali **perrhenites** Na_2ReO_3 and K_2ReO_3 are formed by fusing ReO_2 with alkali hydroxides.

Rhenium forms **sulphides** Re_2S_7 , ReS_2 , and **selenides**, Re_2Se_7 and ReSe_2 . The quantitative precipitation of Re_2S_7 by H_2S from a hot solution in concentrated hydrochloric acid is a method of determination. **Thioperrhenic acid** exists in solution and TlReS_4 as a solid.

TECHNETIUM

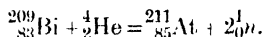
The artificial radioactive element technetium, At. No. 43, fills the place in the periodic table between manganese and rhenium in the sub-group (a) of Group VII. It is obtained in the form of several isotopes in various ways, e.g. by bombarding molybdenum with deuterons (Perrier and Segré, 1937):



The element has most of the properties of rhenium, except that it does not volatilise on heating in sulphuric acid solution in a current of hydrogen chloride gas. The sulphide Tc_2S_7 (which has a formula resembling that of Re_2S_7) is dark brown. The ion TcO_4^- is pink. The metal is isomorphous with rhenium, ruthenium, and osmium.

ASTATINE

Element No. 85 in sub-group (b) of Group VII is an artificial radioactive element called astatine. It is formed by bombarding bismuth with helium ions:



It behaves as a halogen, existing as the free element in solution, from which it is extracted (like iodine) by benzene. The element in solution is reduced by sulphur dioxide and is oxidised by bromine. Astatine is more electro-positive than the halogens and is precipitated along with mercury and bismuth by hydrogen sulphide.

CHAPTER XLVI

GROUP VIII METALS : IRON

GROUP VIII comprises the *inert gases* with completed 8-electron outer shells, and the three triads of Mendeléeff's *transitional elements* :

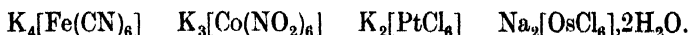
Group VIII a

	At. No.	Electron configuration	Density	At. Vol.	M. Pt.	B. Pt.
{ Iron -	- 26	2·8·14·2	7·86	7·1	1539°	2450°
{ Cobalt -	- 27	2·8·15·2	8·8	6·7	1478°	2900°
{ Nickel -	- 28	2·8·16·2	8·8	6·7	1452°	2900°
{ Ruthenium -	44	2·8·18·15·1	12·26	9·6	2450° >	2700°
{ Rhodium -	45	2·8·18·16·1	12·4	9·8	1970° >	2500°
{ Palladium -	46	2·8·18·18·0	11·9	8·96	1553°	2200°
{ Osmium -	76	2·8·18·32·14·2	22·48	8·5	2750° >	5300°
{ Iridium -	77	2·8·18·32·15·2	22·42	8·6	2440° >	4800°
{ Platinum -	78	2·8·18·32·17·1	21·4	9·1	1755°	4300°

The atomic weights in these triads are more nearly alike than in other parts of the periodic table. These are really central triads in periods of transitional elements in the wider sense (p. 370), there being a gradation of properties along each period, as Mendeléeff already pointed out :

Cr	Mn	Fe	Co	Ni	Cu	Zn
Mo	Tc	Ru	Rh	Pd	Ag	Cd
W	Re	Os	Ir	Pt	Au	Hg

The resemblance between Fe, Co, Ni and the platinum metals from Ru to Pt is not very close, and is seen mainly in the marked tendency to form complex compounds, which nickel shows in a much smaller degree :



There are some resemblances in the vertical groups Fe, Ru, Os ; Co, Rh, Ir ; and Ni, Pd, Pt, but on the whole this is much less important than in other groups of the periodic system.

The platinum metals in their generally " noble " character, tendency to complex formation, and high densities, show analogies with gold. They are all paramagnetic, palladium in the highest degree ; Fe, Co and Ni are ferromagnetic. All the metals have high m.pts.

As transitional elements, the metals of Group VIIIa show a large number

of valencies, the valency suddenly dropping to zero with the inert gases of Group VIIIb. The valencies are :

Fe	1, 2, 3, 6	Ru	1, 2, 3, 4, 5, 6, 7, 8	Os	2, 3, 4, 6, 7 (?), 8
Co	1, 2, 3, 4	Rh	1, 2, 3, 4, 6	Ir	1, 2, 3, 4, 5, 6
Ni	1, 2, 3, 4	Pd	1 (?), 2, 3, 4	Pt	1, 2, 3, 4, 6

the predominating valencies being in heavy type. The appearance of the maximum valency of 8 (the typical valency of the group) in the case of ruthenium and osmium is noteworthy, as is the trivalency of ruthenium and rhodium and the bivalency of palladium, in the common compounds.

Iron, cobalt and nickel oxidise on heating in air and decompose steam at a high temperature, nickel much less readily than iron and cobalt. The monoxides $M^{II}O$ are quite strong bases, the sesquioxides $M^{III}O_3$ are much less basic and are amphoteric : the corresponding salts are stable only in the case of iron, Fe_2O_3 forming *ferrites* such as $Na_2Fe_2O_4$. The oxides M_3O_4 are of the type $M^{II}O, M^{III}_2O_3$ or $M^{II}(M^{III}O_2)_2$, i.e. spinels (p. 811). Iron forms *ferrates* derived from an unknown acidic trioxide $Fe^{VI}O_3$ which resemble chromates and manganates ; K_2FeO_4 , K_2CrO_4 , K_2MnO_4 . The metals iron, chromium and manganese are similar in physical properties.

The order of the elements iron, cobalt, and nickel in the first transition period is in the reverse of that of the atomic weights in the case of cobalt and nickel (p. 369), but agrees with many chemical properties. Cobalt resembles iron, and nickel copper, which follows it in the long period (p. 912). The ease of reduction of the oxides increases in the order Fe, Co, Ni and Cu, and hence the action of the heated metals in decomposing steam follows the reverse order, nickel and copper reacting only at very high temperatures. Nickel tends to form stable compounds in which it is bivalent, and so resembles copper and palladium (vertically below it in the Periodic Table) ; whilst iron, cobalt, ruthenium and rhodium show a tendency to form compounds in which they are trivalent (cobalt in the very stable cobaltamines, etc., but not in the simple salts). The tendency to form complex compounds in which they are trivalent is strong with iron and cobalt, but lacking with nickel.

Iron, cobalt, nickel, ruthenium, iridium and osmium form covalent *carbonyls* with carbon monoxide (p. 950). These compounds bear no relation to the normal valencies of the metals and are chiefly but not always formed by donation of electrons from the carbon monoxide molecules : $Me \leftarrow C \overset{\cdot\cdot}{\underset{\cdot\cdot}{\parallel}} O$.

IRON

History.—Metallic iron was known in pre-dynastic Egypt (before 3400 B.C.) but was exceedingly scarce and used only as beads for jewellery (Flinders Petrie). It may have been obtained from meteoric iron since it contains nickel. Iron of this early period is also known for Mesopotamia, some possibly terrestrial. The metal came into general use in Egypt only

much later (about 1500 B.C.) The use of iron seems to have spread from the Hittites in Asia Minor. It was much used by the Assyrians about 600 B.C. In the Mycenaean (pre-Classical Greek) period described by Homer, iron was still a rare metal—a lump of iron is the prize given to Achilles (*Iliad*, xxiii, 834)—but the Greeks brought with them the use of iron. The Etruscans worked the mines of Elba, later taken over by the Romans who also worked the mines of Spain and Noricum. Iron seems to have been worked at a fairly early date in India and perhaps in China.

Occurrence.—Iron does not occur to any great extent in the free state on the earth, although meteorites, which sometimes consist of metallic iron with from 3 to 30 per cent of nickel and some occluded hydrogen, indicate that it must be present in the solar system.

Meteorites may also consist partly or principally of silicates (*e.g.* olivine) and of glassy minerals (moldavite), although grains of metallic iron are usually present even in stony varieties. On account of the presence of nickel, meteoric iron does not easily rust in moist air. Cobalt, graphite (sometimes small diamonds), ferrous sulphide, *schreibersite* (Fe,Ni,Co)₃P and *cohenite* (Fe,Co,Ni)₃C, not known to exist on the earth, also occur in meteorites. Meteoric dust consisting chiefly of iron is constantly falling on the earth from space, although its presence is noticed only on the surface of the otherwise unsullied snows of the polar regions.

Large masses of native iron, which may be meteoric or have been formed by the reduction of ores in burning coal-mines, occur in Disko Island, West Greenland, and grains of iron in basalt rocks at Giant's Causeway and elsewhere. The inner core of the earth has been supposed to be largely metallic iron. Iron compounds occur in the soil, in green plants, and in haemoglobin (0.336 per cent Fe) the red colouring matter of blood.

Iron ores are plentiful but few in number, although iron occurs in nearly every mineral. The most important ores are the oxides. Ferroso-ferric oxide Fe₃O₄ occurs as the important ore *magnetite* (so-called because certain varieties, lodestone, are permanently magnetic): this is not found to any extent in the British Isles but occurs in Lapland, Sweden, Siberia (Urals), Germany, India (Madras) and North America. It contains 72.4 per cent of iron and is the richest ore. Ferric oxide Fe₂O₃ occurs as *haematite*, sometimes crystalline and red, or if black giving a red streak on unglazed porcelain. It also occurs in earthy, granular and nodular forms, and is found in England in the Furness district in Lancashire and near Whitehaven, in Belgium, Westphalia, Sweden, the Island of Elba, south of Lake Superior and near St. Louis (Missouri). Hydrated ferric oxide, *limonite*, occurs in kidney-shaped masses in South Wales, the Forest of Dean, France, Germany, Bilbao in Spain, and Canada. The *bog iron ores* are hydrated ferric oxides, and occur in large quantities in Ireland, Sweden, and North Germany. The only remaining important ore is ferrous carbonate FeCO₃, occurring alone as *siderite*, *chalybite*, or *spathic iron ore*, in the Alps and in Hungary or mixed with clay as *clay-ironstone*, or with clay and coal as *blackband ironstone*. The hydrated oxide and the impure forms of the carbonate are the most important British ores. Pyrites cinders, chiefly ferri-

oxide, from the manufacture of sulphuric acid are desulphurised by roasting and smelted for iron. The value of an ore of iron depends on its freedom from impurities (S, P, As, etc.), which are detrimental to the resulting metal.

The metallurgy of iron.—The extraction of iron from the ores involves a number of processes.

(1) **Preliminary roasting or calcination** is carried out by stacking the ore with a little coal in heaps or shallow kilns or shaft-furnaces, and regulating the temperature and supply of air so that most of the moisture, carbon dioxide, sulphur and arsenic are expelled; ferrous oxide (FeO) is also converted into ferric oxide (Fe_2O_3) to avoid the production of ferrous silicate in the slag during smelting. The ore is also rendered more porous. Powdery ore is agglomerated by sintering or briquetting.

(2) **Smelting or reducing the ore with carbon in the blast-furnace.**

The blast-furnace (introduced in a simple form about 1500) consists (Fig. 386) of an outer shell of steel plates, lined with refractory bricks. It is 50 to 100 ft. high, the greatest width being up to 24 ft. at the

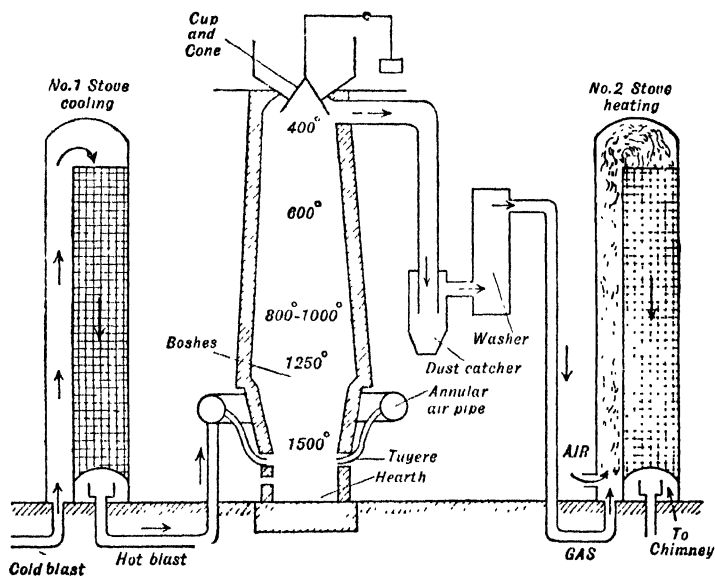


FIG. 386.—Blast-furnace and Cowper stoves.

“boshes”. The mouth is closed with a *cup-and-cone* through which the charge of ore, limestone and fuel is fed intermittently by lowering the cone. (In large modern furnaces a double cup-and-cone is used, which prevents the escape of gas on opening the lower cone.) The gas passes away through a pipe to a *dust-catcher* and *washer* and is utilised by burning in the Cowper stoves (see below) for heating the air-blast. The furnace below the boshes narrows gradually to a *hearth* at the base, pierced with holes for a number of water-jacketed iron blowing-pipes

or *tuyeres*, through which air is forced from an annular pipe by powerful blowing-engines. The hearth is also pierced with a hole stopped with clay from which the molten iron is periodically tapped into sand moulds on the ground, and a *slag-notch* at a higher level through which the molten slag runs continuously from above the fused metal. About 3 to 5 tons of air are passed through the furnace per ton of iron made, the power for working the blowing-engines being supplied by coke-oven gas obtained in producing the coke for the blast furnace. Coal is used in Scotch furnaces but elsewhere hard oven-coke or sometimes charcoal is employed. The use of coke was introduced in 1709 by Darby at Coalbrookdale in Shropshire.

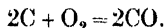
The charge for the blast-furnace consists of 1 ton of coke, 8 to 12 cwt. of limestone to form the slag (consisting of calcium and aluminium silicates) and so much ore (say $2\frac{1}{2}$ tons) as produces 1 ton of iron. The process is continuous and goes on day and night without interruption. Each furnace may produce 300 tons of iron daily.

The air for the blast is pre-heated to 700° to 800° by passing through *Cowper stoves* consisting of tall iron cylinders lined with firebricks, packed with chequer brickwork with a circular gas flue on one side. Part of the gas from the blast-furnace together with sufficient air to burn it passes through until the bricks are red-hot. The products of combustion escape to a chimney (not shown). The gas is then turned through a second stove, and the air blast to the tuyeres is sent through the first one until the brickwork has cooled. The two stoves are thus alternately used as absorbers and emitters of heat, or as heat-regenerators. This economises fuel and the blast-furnace works at a higher temperature.

The blast-furnace gas consists of nitrogen and carbon monoxide with some carbon dioxide; the normal volume composition is N_2 60, CO 24, CO_2 12, H_2 and CH_4 4. It is mostly used in heating the stoves, although in some works it is partly used to raise steam for the blowing-engines or as fuel for gas engines.

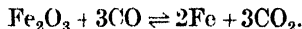
In some cases a *dry blast* is used, the air being first dried by refrigeration or by adsorbing moisture in silica gel. In this way loss of heat by the reaction: $C + H_2O \rightleftharpoons CO + H_2$ in the blast-furnace is prevented.

Chemical reactions in the blast-furnace.—The oxygen of the blast unites with carbon at a very high temperature in the hearth to produce largely carbon monoxide, which rises through the furnace:



The temperature of the charge passing down the furnace increases continually from the mouth to the hearth.

Above the boshes at a dull-red heat the ferric oxide is reduced by carbon monoxide to spongy iron:

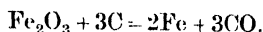


The reaction is reversible and the escaping gas contains both CO and CO_2 in the ratio 1 : 0.5. In this upper zone the limestone is decomposed

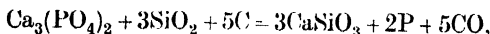


and some carbon dioxide is reduced to monoxide: $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$. The spongy iron absorbs sulphur from the fuel.

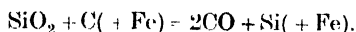
Near the centre of the furnace, at a bright-red heat, finely-divided carbon is deposited by the reaction: $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$. This and the carbon of the charge complete the reduction:



Phosphorus is produced by reduction of phosphates in the ore:



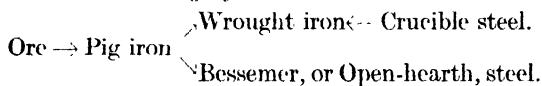
and the phosphorus is absorbed by the iron. At a higher temperature some silicon is formed by the reduction of silica by carbon in presence of iron, and alloys with the iron:



The silica and lime now form a fusible slag which usually contains some calcium sulphide. Manganese is also formed by reduction of manganese compounds in the ore, *e.g.* $\text{Mn}_2\text{O}_3 + 3\text{C} = 2\text{Mn} + 3\text{CO}$.

At a white heat in the lowest part of the furnace the spongy iron containing carbon, silicon, manganese, sulphur and phosphorus fuses to molten cast iron which is tapped off from time to time into sand moulds to form pig iron, or is sent in the fused state to the steel furnaces.

Three varieties of commercial iron are: (1) cast iron or pig iron; (2) malleable iron or wrought iron, (3) steel. The order in which they are prepared from the ore is roughly as follows:



Cast iron.—*Pig iron* contains 2.2 to 4.5 per cent of carbon, with silicon, manganese, sulphur and phosphorus. When the cooling is rapid, the silicon content small and the manganese high, *white pig iron* is formed in which all the carbon is in the form of iron carbide Fe_3C (*cementite*); it is brittle and coarsely crystalline, and dissolves nearly completely in dilute hydrochloric acid evolving a mixture of hydrogen and hydrocarbons. If, however, the molten iron containing at least 2.5 per cent of silicon is slowly cooled most of the carbon separates in the form of fine laminae of graphite, the iron at the same time becoming softer and of a finer texture; on solution in hydrochloric acid it evolves chiefly hydrogen and leaves a black residue of graphite. This variety of cast iron is known as *grey pig iron*. An intermediate variety is called *mottled pig iron*. The solubility of carbon in pure iron is 4.25 per cent, but much more is dissolved if manganese is present.

Malleable or wrought iron.—This is nearly pure iron containing only from 0.12 to 0.25 per cent of carbon, and melts at a higher temperature (1400°–1500°) than cast iron. Malleable iron contains less than 0.5 per cent of total impurities (carbon, sulphur, phosphorus and silicon).

Malleable iron is obtained from cast iron by the **puddling process** invented by Henry Cort of Lancaster in 1784. The cast iron is fused in a

reverberatory furnace (p. 719) the hearth of which is lined with haematite which oxidises the carbon : $3C + Fe_2O_3 = 2Fe + 3CO$, the carbon monoxide bubbling through the molten iron. Sulphur, phosphorus and silicon are oxidised and pass into the slag. When the metal becomes pasty it is formed into lumps or "blooms" which are beaten under steam hammers to squeeze out the slag. The iron although not fused *welds* together to a coherent mass at a bright red-heat.

Malleable iron is tough and fibrous ; its property of welding, whereby two pieces when heated to redness unite on hammering, is exceedingly valuable and is applied in various ways by the blacksmith. Its softness is not appreciably altered by heating to redness and quenching in water, whereas steel then becomes very hard. Wrought iron has now largely been replaced by mild steel.

Wrought iron containing combined phosphorus is brittle at the ordinary temperature and is said to be *cold-short* ; combined sulphur, probably FeS, renders the metal brittle at a red heat, when it is known as *red-short*.

If cast iron is cast in a metal mould so as to cause rapid cooling the cementite may be decomposed by heating the casting, embedded in haematite, for several days. The combined carbon in the surface is oxidised and that from the interior diffuses out to replace it. Finally the carbon content is reduced to that of steel, and a *malleable casting* is produced. Sometimes the cementite in the interior is caused to decompose with separation of fine graphite and the iron becomes soft. The result is a "black-heart casting", white outside with a black core.

Steel.—This is iron which has been fused in the process of manufacture and contains from 0.15 (very soft steel) to 1.5 per cent or more (very hard steel) of carbon, part at least combined with iron or in solid solution. It also contains small amounts of other elements but the impurities of the cast iron, viz, silicon, phosphorus, sulphur and manganese, have mostly been removed.

Analyses of cast iron and the steel made from it illustrate thus :

	Fe	C	Si	P	Mn	S
Cast iron	- 93.2	1.0	1.4	2.5	1.8	0.1
Steel	- 99.3	0.18	0.004	0.02	0.4	0.0024

Steel also differs from iron in acquiring a "temper" by heating and quenching ; it becomes soft when heated and slowly cooled.

Steel may be made (1) from pure wrought iron by increasing the amount of combined carbon, (2) from cast iron by removing part of the carbon and taking out the impurities. In modern processes the second method is used and the main processes are :

- (1) The Bessemer process (Henry Bessemer, 1855).
- (2) The Siemens-Martin or open-hearth process (1864).

When wrought iron is made from pure oxide ores by reduction with charcoal it is converted into steel by the *cementation process*. Bars of

wrought iron surrounded with charcoal are heated for one or two weeks. Absorption of carbon occurs, the carbonisation spreading slowly through the mass and converting the iron into steel. The surface of the bars is covered with blisters, and the blister steel is fused in plumbago crucibles to form *cast steel* or *crucible steel*. This process has been superseded by the electric furnace for high-quality steels for tools, etc.

The Bessemer process.—In this, molten pig iron from the blast-furnace is run into a *converter* (Fig. 387), a large pear-shaped iron vessel lined with refractory silica bricks. The converter holds 10 tons of metal and is supported on trunnions, cold air being forced by a pipe to a hollow perforated bottom from which it bubbles through the molten metal. The charging is carried out through the open mouth with the converter horizontal, and blowing is begun. The converter is then swung into a vertical position and blowing continued.

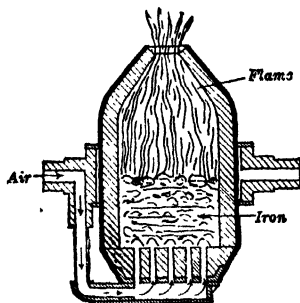


FIG. 387.—Bessemer converter.

Silicon and manganese are first oxidised (producing most of the heat) and pass into the slag, and then part of the iron is oxidised. The resulting ferric oxide removes the carbon, forming carbon monoxide which is now freely evolved and burns at the mouth of the converter as an orange-yellow flame edged with blue and shot through by showers of sparks. After six to eight minutes the flame sinks, indicating that all the carbon has been removed. The converter is again tilted, the blast is stopped, and the requisite amount of spiegel added. *Spiegeleisen* is iron containing manganese and carbon. The converter is blown again for a short time to mix the charge, when the manganese reduces any ferrous oxide and the carbon unites with the iron to form steel. This process of carburising the iron was introduced by Mushet in 1856.

By tilting the converter, the molten steel is poured from it into ladles supported by travelling cranes, from which it is poured into moulds. A little aluminium, silicon-iron alloy (*silicon-spiegel*), or titanium-iron alloy, may be added to prevent blow-holes in the castings due to bubbles of gas (nitrogen, carbon monoxide) which will combine or react with the aluminium, silicon or titanium. According to the percentage of carbon added, various kinds of steel are produced: *tool steel* (0.9 to 1.5 per cent C), *structural steel* (0.2 to 0.6 per cent C) and *mild steel* (0.2 per cent or less C).

Ores of iron containing phosphates give "cold-short" iron. Such "phosphatic ores" are worked by the **Thomas and Gilchrist process** (1879), in which the silica ("acidic") lining of the converter is replaced by a "basic" lining of magnesia and lime prepared by calcining dolomite. Limestone is first charged into the converter along with coke and the blast is turned on. Molten pig iron is run in and the blast continued. Silicon and manganese burn out first and then the phosphorus (pro-

ducing most of the heat) and carbon are oxidised simultaneously. When the carbon is burnt out the flame drops but the blast is prolonged to burn out the remaining phosphorus. The phosphorus pentoxide combines with the lime from the limestone added (*not* the converter lining) to form a slag. Spiegeleisen is added in the ladle (*not* in the converter). The slag ("basic slag") contains calcium phosphate and is used as a fertiliser.

The steel pigs produced by casting are annealed in underground furnaces ("soaking pits") heated by blast-furnace gas, and are then passed through the rolling mills for the production of steel bars.

The open-hearth process.—This was suggested by Réaumur in France in 1722 and by John Payne in 1728 but was first successfully worked in 1864 by the brothers Martin in France, who used the regenerative heating process of Sir William Siemens. It is carried out on a large flat hearth enclosed in a furnace (Fig. 388) heated by producer gas. The air

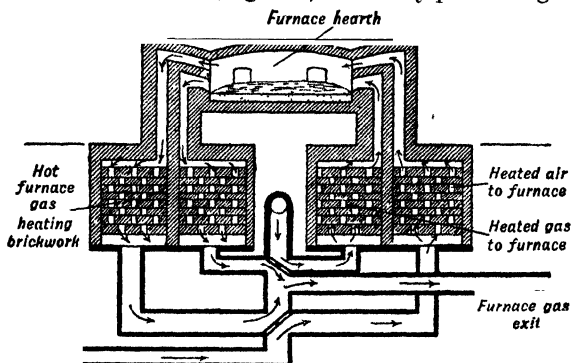


FIG. 388.—Open-hearth steel furnace.

and gas are supplied through separate regenerators of chequer brickwork used in pairs and traversed alternately by the hot products of combustion, and the gas and air, as in the Cowper stoves. The hearth is lined with silica in the "acid" process or with calcined magnesite or dolomite in the "basic" process. The charge consists of pig iron (part of which may be run in liquid from the blast-furnace), steel scrap and haematite, with limestone in the basic process. By the action of the haematite part of the carbon is burnt out of the cast iron and fluid steel remains. The subsequent operations are the same as in the Bessemer process. The furnace may be made to tilt and discharge a portion of its contents into a ladle. The operation lasts 8 to 10 hours; it is more easily controlled than the Bessemer process and is very largely used in Great Britain, although the Bessemer process holds its own elsewhere.

The open-hearth process uses a large quantity of fuel for heating (the thermal efficiency is about 20 per cent), and requires steel scrap equal to about half the weight of the finished steel.

A very pure (*Armco*) iron containing less than 0.1 per cent of total impurity is made by a modification of the open-hearth process. It is almost rustless.

Electric furnaces are used in the production of special high-quality steels. They are mostly on the arc principle and consist of refractory crucibles containing two (or more) large vertical carbon electrodes between which an electric arc is struck. Such furnaces are more especially used for the production of *alloy* steels, containing nickel, chromium, vanadium and molybdenum.

The properties of steel.—The properties of steel depend largely on the content of carbon and the heat-treatment: low-carbon steels are soft like wrought iron and are known as *mild steel*; with more carbon the ductility falls, whilst the tensile strength increases up to the limiting percentage of 1.5 of carbon. Wrought iron and steel are malleable and may be welded. The melting point of steel is lower than that of wrought iron.

The properties of steel depend on the *heat-treatment* to which the metal has been subjected. If steel is heated to redness and quenched in cold water it becomes as hard and brittle as glass. If it is now heated to various temperatures the resulting metal possesses properties depending on the temperature. This operation is known as *tempering*, and the temperature is judged by the colour of the thin film of oxide produced on a bright surface of the metal.

230° : light-straw colour : used for razor blades.

255° : brownish-yellow : used for penknives and axes.

277° : purple : used for cutlery.

288° : bright-blue : used for watch-springs and swords.

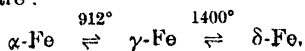
290°–316° : dark-blue : used for chisels and large saws.

Wrought iron is *case-hardened* by heating in contact with carbon or potassium ferrocyanide, etc., when a surface-layer of steel is formed. *Armour plate* is made by case-hardening a sheet of soft steel on one side and spraying with cold water when red-hot. Nickel-chromium steels form very tough armour plate and after heat-treatment are used for projectiles. A very hard surface, used for cylinder bores, etc., is formed by *nitriding*, i.e. heating steel containing about 1 per cent of aluminum at 450°–500° in an atmosphere of ammonia. Iron nitrides (Fe₂N, etc.) are formed in the interstices of the iron crystals and prevent gliding of the latter under stress.

Allotropic forms of iron.—Three allotropic forms of pure iron are recognised.

- (i) α -iron (or α -ferrite), stable below 912°, soft, magnetic, able to dissolve only a little carbon, crystallising in a body-centred cubic lattice (p. 390); the chief constituent of pure wrought iron.
- (ii) γ -iron (or γ -ferrite), stable from 912° to 1400°, non-magnetic, dissolving carbon to form a solid solution, crystallising in a face-centred cubic lattice.
- (iii) δ -iron (or δ -ferrite), stable above 1400°, does not dissolve carbon, crystallising in a body-centred cubic lattice and perhaps the same as α -iron.

The phase changes are :



Iron loses its ferro-magnetism at about 760° but this is not due to an allotropic change into a β -iron as was once thought. When α -iron changes into γ -iron the length of the lattice cube side increases, but as there are more iron atoms in the γ -iron cube the net result is actually a contraction.

The iron-carbon system.—When steel containing carbon and also nickel or manganese is heated and quenched it forms a homogeneous non-magnetic solid solution of carbon in γ -iron called *austenite*, with a structure of relatively soft large crystals. Nickel or manganese retards the conversion of γ - into α -iron which would otherwise occur below 912° and would form a heterogeneous mixture of soft α -iron and hard grains of iron carbide or *cementite*, Fe_3C .

Cementite forms rhombic crystals, insoluble in dilute acids, so that it can be isolated from steel by the action of dilute sulphuric acid and potassium dichromate. A carbon steel not stabilised by manganese or nickel forms on heating and quenching a very hard steel with a needle-like structure and tetragonal lattice, called *martensite*, which is a primary metastable stage in the breaking down of austenite into α -iron and cementite. The formation of martensite is co-extensive with hardness in the steel.

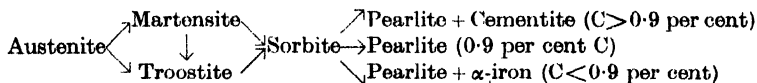
Less rapid cooling of iron containing only a little carbon forms a mixture of crystals of α -iron and *pearlite*, a finely laminated eutectoid structure (see below) of alternate layers of α -iron and cementite, with an average carbon content of 0.9 per cent and formed at 695° .

Hard martensitic steel is formed only on cooling faster than a critical hardening speed, which is very high for carbon steels but much smaller for alloy steels, which can sometimes be hardened even by air-cooling. If the steel is cooled rapidly but below the critical hardening speed it forms *troostite*, another transitional material from the breakdown of austenite into pearlite, but formed at a much higher temperature than martensite. It is formed on cooling heated carbon steels in oil and is about half as hard as martensite, from which it can also be formed.

Another transitional stage in the less rapid cooling of a steel containing manganese is *sorbite*, which has a very finely laminated pearlite structure with great tenacity and ductility; it is best produced by first hardening and then tempering at about 650° .

The structure of a hardened and fully tempered steel consists of small spherical particles of the very hard cementite Fe_3C uniformly distributed in a soft ferrite (iron) matrix; it is often called *true sorbite* and has great tenacity and ductility.

According to the carbon content, pearlite or mixtures of pearlite with cementite or with α -iron (ferrite) may be formed. When very slowly cooled the cementite breaks down into soft α -iron and scales of graphite:



In Fig. 389, *A* is the m.p. 1539° of pure iron (δ -iron). This is lowered by the presence of dissolved carbon along the liquidus curve *AB*, a solid solution of carbon in δ -iron separating. (The curves corresponding with liquid solution phases are called *liquidus curves*, those corresponding with solid solution phases in equilibrium with the liquids are called *solidus curves*).

At *B* a transition occurs, and along *BC* austenite, a solid solution of carbon in γ -iron, separates. The transition point of δ -iron into γ -iron is shown on the vertical axis at 1400°. *DE* is the solidus curve for austenite, and represents the lowering of m.pt. due to the solution of carbon in solid iron. *C* is a eutectic point (1125°) at which the mass solidifies to a mixture of austenite and cementite (Fe_3C). The curves show that molten iron containing less than 1.8 per cent of carbon may solidify entirely to austenite, whilst liquids containing more than 4.3 per cent of carbon deposit cementite. *CH* is the solubility curve of cementite.

When the solid iron cools further, the solubility of carbon in γ -iron decreases, and cementite deposits from the solid. The percentage of carbon in solution in the austenite decreases along *EF*, the point *F* corresponding with 0.87 per cent of carbon. At 912° the γ -iron changes to α -iron, which does not form a solid solution with carbon. The carbon dissolved in γ -iron depresses the transition point of γ -iron into α -iron along *GF*, *F* being called a *eutectoid point* where the remaining austenite is converted into a mechanical mixture (*eutectoid*) of α -iron and cementite, viz. *pearlite*. Below 700° no further phase-changes occur.

Alloys with less than 0.87 per cent of carbon are called *hypoeutectoid alloys*, those with between 0.87 and 1.8 per cent *hypereutectoid alloys*. The alloy at *C* with 4.3 per cent of carbon is the *eutectic alloy*, those with 1.8 to 4.3 per cent are *hypoeutectic*, and those with 4.3 to 5 per cent of carbon are *hypereutectic* alloys.

When graphite separates instead of cementite, as sometimes occurs on very slow cooling, the points *E* and *C* are raised to *E'* and *C'*, and *C'H'* is the solubility curve of graphite. It intersects *BC* at 1137°. The magnetic transformation at about 760° is not a phase-change. The thermal change taking place in it is the cause of *recalescence*, the sudden reheating of a mass of red-hot iron on slow cooling.

Pure iron.—The soft iron wire used for binding flowers contains 99.7 per cent of iron. *Armed iron* (p. 920) is 99.9 per cent Fe. Very pure iron is difficult to make. It may be obtained by reducing pure ferric oxide (made by heating recrystallised ferric nitrate) in hydrogen at 1000°, or by electrolysis of a solution of ferrous sulphate or chloride, or ferrous ammonium sulphate, and melting in a vacuum. Pure iron is soft and almost white. It is permeated by hydrogen at about 350°, the

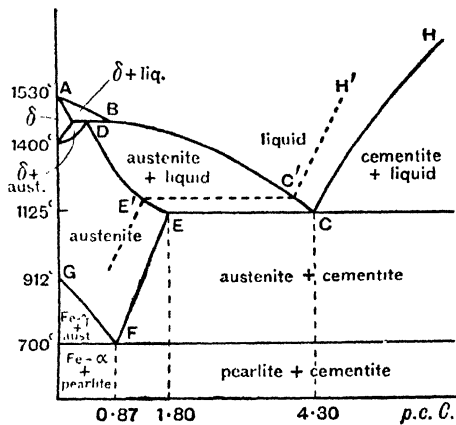


FIG. 389.—The iron-carbon system.

permeability increasing rapidly up to a red heat, and it burns brilliantly in oxygen when heated.

Carbonyl iron in fine powder is made by injecting iron carbonyl $\text{Fe}(\text{CO})_5$ vapour into a space heated by radiant heat at $200^\circ\text{--}250^\circ$. It is quite pure except for traces of carbon and oxygen. By fusing in an induction furnace with the requisite amount of pure ferric oxide (obtained from iron carbonyl) the carbon may be reduced below 0.0007 per cent and the oxygen below 0.01 per cent. Iron powder may be pressed with an adhesive into *Pupin coils*, with very low hysteresis loss and used in some electrical apparatus.

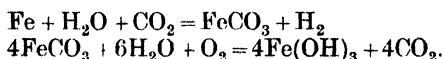
Electrolytic iron is brittle because of its fine crystalline structure and can be powdered. It contains occluded hydrogen which can be removed by heating in vacuum, when the metal also becomes soft by annealing. Hydrogen penetrates heated iron and steel, and removes carbon, sulphur and phosphorus, the metal becoming soft. *Reduced iron* is a black or grey powder obtained by heating ferric oxide in hydrogen; when prepared from pure oxide (from the nitrate by reduction at a fairly low temperature) it is pyrophoric.

Iron readily occludes hydrogen, nitrogen and carbon monoxide, the solubility increasing with rise in temperature and showing a marked alteration about 936° . The excess of gas is liberated on cooling the molten metal, and that retained by the solid is removed by heating in a vacuum.

Iron does not easily amalgamate with mercury, but an amalgam is obtained by rubbing iron powder with mercuric chloride and water, or by the action of sodium amalgam on ferrous chloride solution: 1 per cent sodium amalgam gives 1.29 per cent iron amalgam.

The rusting of iron.—Iron exposed to ordinary moist air is quickly corroded to a reddish-brown rust, consisting chiefly of hydrated ferric oxide. The conditions under which rusting takes place have been investigated by several experimenters, with divergent results. The homogeneity or otherwise of the metal and its purity affect the results. The presence of water is essential and according to some experimenters carbon dioxide or acidity is also necessary. Freshly-formed rust usually contains ferrous hydroxide and carbonate, indicating that these compounds may be formed as a first step in the corrosion.

Crace Calvert (1876) and Crum Brown (1888) suggested the following reactions:



According to G. T. Moody (1906), pure iron does not rust in the presence of water and air if carbon dioxide is rigorously excluded. The iron first passes into solution, when carbon dioxide is present, as ferrous bicarbonate $\text{Fe}(\text{HCO}_3)_2$, which is then oxidised by dissolved oxygen with precipitation of ferric hydroxide. The addition of alkalis to the water removes the carbonic acid and retards the rusting of iron.

Lambert (1910) found that pure iron remains bright in distilled water exposed to pure air but rusts if previously mechanically strained.

Take four lots (*a*), (*b*), (*c*), (*d*), of clean bright nails.

(*a*) Boil tap-water in a test-tube until it begins to "bump," showing that dissolved air has been expelled. Drop the nails (*a*) into the water and boil again for half a minute. Pour melted vaseline over the surface of the water. This excludes air, so that iron and water alone are present.

(*b*) Place nails (*b*) in a test-tube full of ordinary water. In this case iron, much water, and air are present.

(*c*) Place nails (*c*) in a test-tube with a few drops of water. In this case iron, a little water, and air are present.

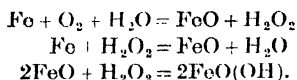
(*d*) Place nails (*d*) in a desiccator over sulphuric acid. In this case iron and air alone are present.

Leave the four specimens for a few days, and examine the iron. Rusting should have occurred only in cases (*b*) and (*c*).

Pour 100 ml. of 15 per cent potassium hydroxide solution into a 500 ml. flask fitted with a partly bored cork and shake. Allow the flask to stand for two days. Boil a large bright nail with distilled water as described above (*a*), and push it through the cork into the flask, leaving a short length outside. Allow to stand for a few days. The part of the nail inside the flask which is exposed to air and water in the absence of carbon dioxide does not rust, whilst the part outside, exposed to moisture and ordinary air will rust. It has been found that even if *liquid* water is condensed on the iron inside the flask it does not rust.

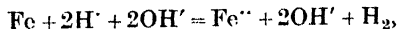
It will be noticed in Expt. (*b*) that the undersides of the nails remain bright, and rust is deposited on the top exposed to air. This indicates that the iron passes into solution, and the solution is then oxidised by the air. Pack a number of bright nails tightly in a jar, cover them with a piece of hardened filter-paper, and pour boiled distilled water into the jar. Rust is deposited *abôve* the filter-paper.

Dunstan, Jowett and Golding (1905) found that iron rusts in moist oxygen in the absence of carbon dioxide. They assumed the reactions :



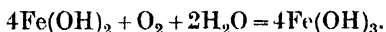
They were unable to detect any H_2O_2 during rusting, but a *trace* is said to be formed by the action of iron amalgam on alkaline solutions (Schönbein ; Wieland and Franke, 1929). Vernon (1935) also found that carbon dioxide is not necessary for rusting and even retards it.

According to another theory of rusting (Thenard, 1819), the different parts of a piece of iron act as poles of voltaic cells and solution of metal occurs as the result of local action. Iron in presence of water is supposed to react primarily as :



and as the process is electrolytic the ferrous and hydroxide ions appear

at two different points ; by diffusion they react with precipitation of ferrous hydroxide, which is then oxidised by dissolved oxygen :



The action of carbonic acid is supposed to be to furnish H^+ ions.

Prepare a 1½ per cent solution of agar-agar in hot water, and add a little sodium chloride and phenolphthalein. Pour some of the solution over a clean plate of iron in a glass dish. The agar sets to a jelly. After some hours red patches appear, indicating the formation of sodium hydroxide by electrolysis. If potassium ferri-cyanide and phenolphthalein are added to the agar and the hot solution is poured over clean iron nails, the anodes become blue from reaction of ferri-cyanide with ferrous ions, and the cathodes red from the alkali formed.

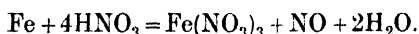
Iron is protected from rusting by painting, or whitewashing with lime. Pipes are protected by heating and dipping into a solution of coal-tar pitch in coal-tar naphtha, when an impervious coating is formed (*Angus Smith's compound*). In the *Barff process* the iron is heated to redness and steam blown over it, when an adherent layer of ferrosoferric oxide is formed. This is used in treating cans for fruit, etc., instead of tinning. The layer of oxide is removed by heating with water containing magnesium chloride, which explains the corrosive action of sea-water on boilers.

Passive iron.—Iron becomes passive by immersion in fuming nitric acid, and also in chloric acid, chromic acid, or hydrogen peroxide, or by making it the anode in electrolysis. The iron is then insoluble in dilute acids and does not precipitate copper from a solution of copper sulphate (Keir, 1790). The passivity is removed by touching with ordinary iron under the surface of dilute sulphuric acid. The passivity, as Faraday (1836) suggested, is due to a very thin film of oxide ; this is removed by heating in hydrogen, and it is possible to dissolve out the iron, leaving the transparent skin of oxide, by iodine solution or by anodic electrolysis in salt solution.

Salts and ions of iron.—Iron readily dissolves in dilute hydrochloric or sulphuric acids, producing ferrous salts, the solutions of which contain the bivalent ferrous ion : $\text{Fe} + 2\text{H}^+ = \text{Fe}^{++} + \text{H}_2$. In cold dilute nitric acid no gas is evolved, but ferrous and ammonium nitrates are formed :



In warm dilute nitric acid iron dissolves to form ferric nitrate with evolution of nitric oxide :

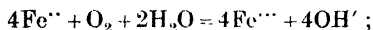


Solutions containing the ferrous ion are nearly colourless, but usually have a green tinge due to traces of ferric ion Fe^{+++} . They have an inky taste and are easily oxidised by atmospheric oxygen, insoluble basic ferric salts being deposited (see below).

The ferric ion Fe^{+++} is nearly colourless, the yellow, red or brown colour of ordinary solutions of ferric salts being due to undissociated compound, basic compounds, or colloidal ferric hydroxide formed by hydrolysis. If these brown solutions are mixed with concentrated

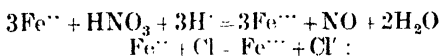
nitric acid they become nearly colourless; with concentrated hydrochloric acid they become deep yellow, the colour of undissociated ferric chloride.

Ferrous salts are oxidised to ferric salts: (i) by atmospheric oxygen in neutral solutions, when insoluble basic ferric salts are precipitated:

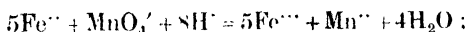


(ii) by chlorine or bromine: $2\text{Fe}^{++} + \text{Cl}_2 = 2\text{Fe}^{+++} + 2\text{Cl}'$; the reaction with iodine is reversible: $2\text{Fe}^{++} + \text{I}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{I}'$; ferric chloride liberates iodine from potassium iodide and iodine oxidises ferrous chloride to ferric chloride:

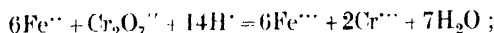
(iii) by boiling with nitric acid or aqua regia:



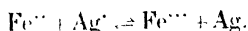
(iv) by permanganate in acid solution:



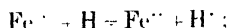
(v) by dichromate in acid solution:



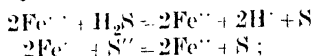
(vi) by silver salts (the reaction is reversible):



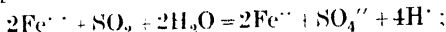
Ferric salts are reduced to ferrous salts (i) by nascent hydrogen in acid solution, say by zinc and dilute sulphuric acid:



(ii) by hydrogen sulphide or sulphides:

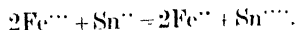


(iii) by sulphur dioxide:



(iv) by iodides: $2\text{Fe}^{+++} + 2\text{I}' \rightleftharpoons 2\text{Fe}^{++} + \text{I}_2$:

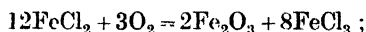
(v) by stannous chloride:



FERROUS COMPOUNDS

Ferrous chloride is obtained anhydrous in white lustrous scales on heating iron in a stream of hydrogen chloride: $\text{Fe} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2$, or by heating ferric chloride in hydrogen: $2\text{FeCl}_3 + \text{H}_2 = 2\text{FeCl}_2 + 2\text{HCl}$. Anhydrous ferrous chloride is also formed by adding ammonium chloride to ferrous chloride solution, evaporating in absence of air, and heating the residue in absence of air till the ammonium salt volatilises. The hydrate is deposited from solutions of iron in hydrochloric acid in bluish-green monoclinic crystals $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, which oxidise slightly and become green in the air.

Anhydrous ferrous chloride is soluble in alcohol and ether. It volatilises at about 1000° and the vapour density indicates that molecules of Fe_2Cl_4 and FeCl_2 are present, the density becoming normal between 1300° and 1500° : $\text{Fe}_2\text{Cl}_4 \rightleftharpoons 2\text{FeCl}_2$. On heating in air oxidation occurs; ferric chloride volatilises and ferric oxide remains:



and when heated in steam, hydrogen is evolved:



Double salts are $\text{RbFeCl}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Cs}_2\text{FeCl}_4 \cdot 2\text{H}_2\text{O}$.

Ferrous bromide FeBr_2 and ferrous iodide FeI_2 are prepared from the elements, and form the crystalline hydrates $\text{FeBr}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeI}_2 \cdot 4\text{H}_2\text{O}$. They are also formed by adding the halogen to iron filings (in excess) and water. Ferrous fluoride FeF_2 is formed as a white powder on heating iron powder or anhydrous ferrous chloride in a stream of hydrogen fluoride. It forms green $\text{FeF}_2 \cdot 4\text{H}_2\text{O}$.

Ferrous oxide FeO is formed as a pyrophoric black powder by reducing ferric oxide with hydrogen at 300° or in a mixture of equal volumes of carbon monoxide and carbon dioxide at 800° ; by heating ferrous oxalate at 150° – 169° in absence of air: $\text{FeC}_2\text{O}_4 \rightarrow \text{FeO} + \text{CO} + \text{CO}_2$ (this contains some iron and is pyrophoric); or by adding ferrous oxalate (obtained by precipitating ferrous sulphate with ammonium oxalate) to boiling potassium hydroxide solution: $\text{FeC}_2\text{O}_4 + 2\text{KOH} \rightarrow \text{FeO} + \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$.

Ferrous oxide always contains iron or Fe_3O_4 : it is prepared nearly pure by heating at 700° small quantities (0.1 gm.) of ferric oxide in a mixture of steam and hydrogen in the ratio 1 : 0.58.

Ferrous oxide melts at 1355° . It is not strongly magnetic. It is reduced to metallic iron by hydrogen at 700° – 800° .

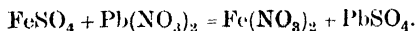
Ferrous hydroxide $\text{Fe}(\text{OH})_2$ is formed as a white precipitate when sodium hydroxide is added to a pure solution of a ferrous salt, with absolute exclusion of air. (To obtain the original solution free from ferric salts, it is warmed with a little iron and dilute sulphuric acid in a flask fitted with a tube dipping under water). It is insoluble in excess of alkali unless the latter is very concentrated, but dissolves slightly in ammonium salts, and is readily soluble in acids, forming ferrous salts. It crystallises from concentrated sodium hydroxide solution in flat green prisms, and is a definite compound. The precipitate rapidly becomes green in the air from formation of Fe_3O_4 , and finally brown, forming $\text{Fe}(\text{OH})_3$. It reduces nitrates and nitrites to ammonia. The solution in very concentrated alkali hydroxide may contain a ferrosite: $\text{Fe}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2\text{FeO}_2 + 2\text{H}_2\text{O}$.

Ferrous carbonate occurs as *siderite* or *spathic iron ore* in rhombohedra isomorphous with calcite. It is formed on addition of an alkali carbonate to a ferrous salt solution as a white precipitate, rapidly becoming green and finally brown on exposure to air, owing to oxidation to ferric hydroxide. The addition of sugar retards the oxidation. Ferrous carbonate dissolves only sparingly in water (10^{-5} gm. mol. per

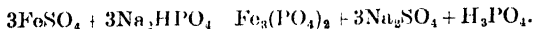
litre) but is soluble in ammonium carbonate solution, and in water containing carbonic acid forming ferrous bicarbonate $\text{Fe}(\text{HCO}_3)_2$, which is sometimes present in springs. On exposure to air, red ferric hydroxide is precipitated: $2\text{Fe}(\text{HCO}_3)_2 + \text{O} = \text{Fe}_2\text{O}_3 + 4\text{CO}_2 + 2\text{H}_2\text{O}$. Plants absorb iron from the soil as the bicarbonate.

Potassium ferrous carbonate $\text{K}_2\text{Fe}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ deposits in nearly white scales from a mixture of potassium carbonate solution and one-fifth the volume of saturated ferrous chloride solution. Impure calcium ferrous carbonate $\text{CaFe}(\text{CO}_3)_2$ is found as *ankerite* in coal measures.

Ferrous nitrate $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ forms light-green crystals, best prepared by grinding ferrous sulphate and lead nitrate with dilute alcohol, filtering and evaporating:



Ferrous phosphate $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ occurs as *vicianite* and is formed as a white precipitate (turning blue in air from oxidation) by precipitating ferrous sulphate solution with sodium phosphate and allowing to stand at 60° – 80° :



Ferrous sulphate FeSO_4 is the most important ferrous salt and is obtained by dissolving iron or ferrous sulphide in dilute sulphuric acid, filtering, evaporating, and crystallising, when green crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ separate. It is made on the large scale by the slow oxidation of marcasite or "coal-brasses," FeS_2 , by air in presence of water (*pyrites* is stable in air unless it is first roasted). The common form is *green vitriol* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, crystallising in monoclinic crystals isomorphous with one form of Epsom salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The pure salt is pale greenish-blue and is made by pressing the powdered crystals between filter paper. If a crystal of *white vitriol* $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is placed in the saturated solution *rhombic* crystals of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, isomorphous with the zinc salt deposit, whilst *blue vitriol* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ induces the crystallisation of *triclinic* isomorphous crystals of $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$. By precipitating a solution with alcohol, or by heating green vitriol in a vacuum at 140° , the white monohydrate $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, is formed; this is stable in air and on heating at 300° in a current of dry hydrogen leaves white amorphous anhydrous FeSO_4 . On heating to redness it decomposes: $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_3 + \text{SO}_2$. Crystalline hydrates with 6, 5, 4, 3 and $2\text{H}_2\text{O}$ are also known.

Ferrous sulphate readily forms double-salts with sulphates of alkali-metals, $\text{M}^1_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, belonging to a group of isomorphous *picromerites* or *schönites*, in which M^1 may be K, Rb, Cs, and NH_4 , ferrous iron may be replaced by bivalent Cu, Mg, Zn, Cd, Mn, Co, and Ni, and sulphur may be replaced by Se, Te, and Cr. If equimolecular amounts of ferrous sulphate and ammonium sulphate are dissolved to saturation in separate amounts of warm distilled water, a little sulphuric acid being added to the ferrous sulphate solution, and the filtered solutions mixed, **ferrous ammonium sulphate** (*Mohr's salt*) $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, deposits on cooling in light bluish-green monoclinic crystals, which

also deposit in the form of a practically white powder on adding alcohol to the solution (*cf.* $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The crystals are stable in air and the solution is much less readily oxidised by atmospheric oxygen than ferrous sulphate or chloride. Mohr's salt is used in volumetric analysis for standardising solutions of potassium permanganate or dichromate. It contains almost exactly one-seventh its weight of ferrous iron. A little dilute sulphuric acid should be added in making the solution.

Iron dissolves in sulphurous acid without evolution of gas: the solution deposits colourless crystals of **ferrous sulphite**, leaving a solution of **ferrous thiosulphate**: $2\text{Fe} + 3\text{H}_2\text{SO}_3 = \text{FeSO}_3 + \text{FeS}_2\text{O}_3 + 3\text{H}_2\text{O}$. (For **ferrous sulphide** see p. 933).

FERRIC COMPOUNDS

Ferric oxide.—There are two crystalline forms of ferric oxide (Robbins 1860): rhombohedral $\alpha\text{-Fe}_2\text{O}_3$ (*haematite*), paramagnetic: and regular $\gamma\text{-Fe}_2\text{O}_3$, ferromagnetic. $\gamma\text{-Fe}_2\text{O}_3$ passes into $\alpha\text{-Fe}_2\text{O}_3$ at about $400^\circ\text{--}700^\circ$. The only definite crystalline **ferric oxide hydrate** (*ferric hydroxide*) is $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, or $\text{OFe}(\text{OH})$, which also exists in two forms, *goethite* or $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (paramagnetic), and *lepidocrocite* or $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (ferromagnetic). The γ -hydroxide loses water at 200° to form the γ -oxide which at 700° passes into the α -oxide: the α -hydroxide at 700° loses water to form the α -oxide.

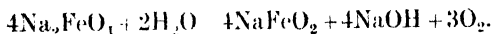
Goethite or $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is obtained artificially as a reddish-yellow precipitate by oxidising ferrous bicarbonate solution with hydrogen peroxide, oxidation of ferrous hydroxide or carbonate in presence of water by atmospheric oxygen, and heating ferric hydroxide gel with dilute alkali in an autoclave. *Lepidocrocite* or $\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is obtained as a bright yellowish-red precipitate by warming a neutral or weakly acid ferrous solution with equivalent weights of sodium thiosulphate and sodium iodate, by precipitating ferrous salts with alkaline hypochlorite, and by oxidising precipitated ferrous hydroxide under special conditions in solution. The mineral *limonite*, formerly regarded as $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, is goethite with adsorbed water.

A brown ferric hydroxide gel is precipitated from a solution of a ferric salt by ammonium chloride and ammonia: it is slimy in the cold but becomes flocculent on boiling. It is soluble in dilute acids but practically insoluble in water and alkalis, and is the form in which iron is separated in quantitative analysis. On prolonged boiling in contact with the solution, the precipitate becomes sparingly soluble in acids. The gel on drying forms a dark-brown amorphous mass of indefinite composition. On ignition this loses water, sometimes with the production of a glow, and $\alpha\text{-Fe}_2\text{O}_3$ is formed, which is nearly insoluble in acids: it dissolves in concentrated hydrochloric acid only after digestion for several days but more easily in presence of ferrous salts. The best solvent is a boiling mixture of 8 parts of sulphuric acid and 3 parts of water. If a current of hydrogen chloride is passed over the strongly-heated oxide, it becomes crystalline. Ferric oxide melts at 1563° . Red varieties of ferric oxide formed by igniting ferrous sulphate in air are used as paints or as a polishing powder (*rouge, crocus, colcothar*).

The stable crystalline form of ferric oxide is steel-grey but gives a red powder. All varieties become brown to dark violet at 650°-1000°; above this temperature they turn bluish-black or black, but when mixed with alumina, Fe₂O₃ becomes yellow on ignition.

Colloidal ferric oxide is known in two forms. (i) *Graham's sol* is obtained by dissolving freshly-precipitated ferric hydroxide in a concentrated solution of ferric chloride and dialysing, preferably hot. The blood-red sol (*dialysed iron*) is a positive colloid and is readily precipitated by salts. Concentrated hydrochloric acid *slowly* converts the solution into yellow ferric chloride. If glycerol, sugar, tartaric acid, etc., are added to a solution of a ferric salt it is not precipitated by ammonia, but a clear brown sol is formed, hence organic matter if present must be destroyed by ignition before the group-reagents of qualitative analysis are used. (ii) *Péan de Sainte-Gilles's sol* is brick-red and is formed by heating a solution of ferric acetate for several days, or by dissolving freshly-precipitated ferric hydroxide in acetic acid, diluting and boiling out the acetic acid.

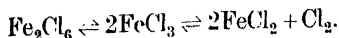
Ferric oxide has feeble acidic properties. If ferric oxide is strongly heated with sodium carbonate, sodium ferrite Na₂Fe₂O₄ or NaFeO₂ is formed: Na₂CO₃ + Fe₂O₃ = Na₂Fe₂O₄ + CO₂. On treating the mass with hot water, the ferrite is decomposed: Na₂Fe₂O₄ + H₂O = 2NaOH + Fe₂O₃ (the old Löwig process, p. 688). Ferrites are sometimes called *perferrites* or *ferrates*. Crystals of sodium ferrite are formed on boiling a solution of sodium ferrate and cooling:



Ferrosferric oxide Fe₃O₄, probably ferrous ferrite Fe(FeO₂)₂, is strongly magnetic and is formed by heating iron to redness in air ("smithy scales") or in steam, or by heating ferric oxide above 1000° in vacuum. The pure oxide is obtained as a black powder by reducing Fe₂O₃ at 400° in a current of hydrogen and steam. It melts at 1540° and is cast into electrodes, since it resists acids and chlorine when fused.

A black hydrated ferrosferric oxide Fe₃O₄.aq is formed when iron filings stand in water exposed to air or by adding a solution containing FeCl₂ + 2FeCl₃ to boiling ammonia, washing and drying. It is strongly magnetic and is soluble in acids. It was formerly regarded as ferrosferric hydroxide Fe₃(OH)₈ · Fe(OH)₂ · 2Fe(OH)₃.

Ferric chloride FeCl₃ is the most important ferric salt. It sublimes in anhydrous iron-black crystals with a green iridescence on heating iron or ferric oxide (at 900°-1000°) in chlorine. The apparatus of Fig. 379 may be used. The crystals sublime at 280° and the vapour density at 44° corresponds with Fe₂Cl₆. At higher temperatures dissociation to FeCl₂ occurs and is practically complete at 750°. At higher temperatures there is some decomposition into ferrous chloride and chlorine:



Temperature	-	448°	518°	606°	750°	1050°	1300°
Δ (H = 1)	-	151	138	121	78	76·3	73·4

In solutions in alcohol and ether the molecular weight corresponds with FeCl_3 . The anhydrous chloride is soluble in benzene. The solutions show the bright-yellow colour of FeCl_3 . Aqueous solutions containing excess of hydrochloric acid are also bright yellow.

Aqueous solutions of ferric chloride are formed by dissolving ferric hydroxide in hydrochloric acid, or by saturating a solution of ferrous chloride with chlorine. On evaporation and cooling, yellow hydrated crystals are deposited which are readily soluble in water. Ferric chloride solution is used as a styptic, *i.e.* in stopping bleeding: it coagulates the blood, forming a clot. The solution is strongly acid, due to hydrolysis (p. 926). On heating the hydrate, hydrochloric acid is evolved and a basic salt or finally ferric oxide is left.

Garnet-red double salts are formed from ferric chloride and other chlorides, *e.g.* $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$; $\text{FeCl}_3 \cdot \text{NH}_4\text{Cl}$; $\text{FeCl}_3 \cdot \text{MgCl}_2 \cdot \text{H}_2\text{O}$.

Fig. 390 is from Roozeboom's experiments. AB is the freezing point curve from pure ice at A to the eutectic of $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and ice at B (-55°). BC is the solubility curve of the 12-hydrate, C being the melting point of this pure hydrate. This is a maximum on the curve, which is characteristic of a definite compound. Beyond C the solution takes up more salt, CD showing the lowering of freezing point by adding ferric chloride. At D a new hydrate $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ appears, its melting point 32.5° being at E . The curve FGH belongs to the hydrate $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ melting at G , and the curve HJK to the hydrate $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ melting at J (73.5°). The curve beginning at K (66°) is the solubility curve of anhydrous

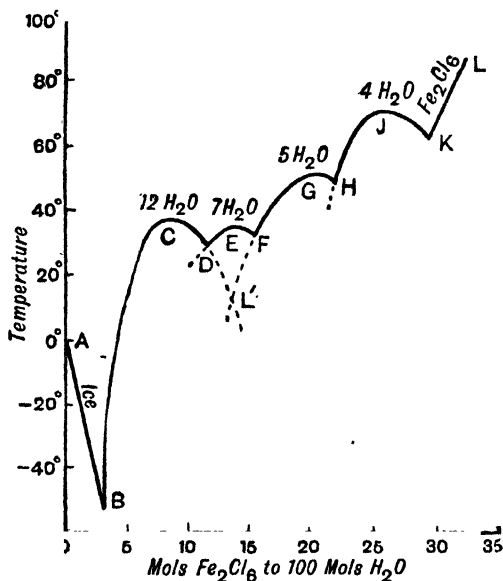


FIG. 390.—Hydrates of ferric chloride.

ferric chloride, which runs up very steeply to a point well off the diagram.

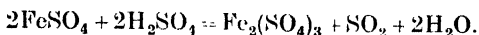
Ferric fluoride FeF_3 is a white sparingly soluble salt and only slightly ionised in solution. It forms double fluorides, *e.g.* Na_3FeF_6 analogous to cryolite. Ferric bromide FeBr_3 is formed similarly to the chloride, but the iodide does not exist.

Ferric nitrate $\text{Fe}(\text{NO}_3)_3$ is obtained by dissolving iron in fairly concentrated nitric acid, or in warm dilute nitric acid: $\text{Fe} + 4\text{HNO}_3 = \text{Fe}(\text{NO}_3)_3$

$\text{NO} + 2\text{H}_2\text{O}$; the dark-brown solution (used as a mordant) deposits colourless or pale-violet cubic crystals of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, or monoclinic crystals of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Ferric phosphate, $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is formed as a white precipitate, insoluble in acetic acid but soluble in mineral acids (except phosphoric) when sodium phosphate is added to a ferric salt solution, or ferric chloride to excess of phosphoric acid solution. It is used in the separation of phosphates in qualitative analysis. A basic phosphate occurs as the mineral *dufrenite* $\text{Fe}_2\text{PO}_4(\text{OH})_3$.

Ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$, is most easily obtained by evaporating ferrous sulphate with concentrated sulphuric acid:

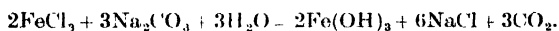


Anhydrous ferric sulphate is a yellowish-white powder, dissolving only very slowly in water but ultimately forming a very concentrated solution. This is brown-red owing to hydrolysis, but becomes paler on addition of sulphuric acid. The common crystal hydrate is violet $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Ferric alums are formed with alkali sulphates *e.g.* $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, violet when pure but often pale-yellow owing to the presence of ferric oxide. These are readily soluble in water and are not appreciably hydrolysed. The potassium alum, $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, does not crystallise so easily as the ammonium salt.

On heating ferric sulphate sulphur trioxide is evolved, the reaction being reversible: $\text{Fe}_2(\text{SO}_4)_3 = \text{Fe}_2\text{O}_3 + 3\text{SO}_3$.

Ferric carbonate does not appear to exist, ferric hydroxide being precipitated by an alkali carbonate from a ferric salt solution:



Sulphides of iron.—There are three sulphides of iron, **ferrous sulphide** FeS and **iron disulphide** FeS_2 , both containing ferrous iron, and **ferric sulphide** Fe_2S_3 .

Ferrous sulphide FeS is formed with evolution of heat as a black mass by heating 3 parts of iron filings with 2 parts of sulphur (p. 10). It may be prepared by dipping a white-hot bar of wrought iron into molten sulphur in a crucible. (Cast iron is not attacked.) A mixture of iron filings and sulphur when moistened becomes heated and forms FeS . The mineral *pyrrhotite* or *magnetic pyrites* is often formulated as Fe_7S_8 but apparently it has a composition varying from Fe_7S_8 to Fe_8S_9 , and artificial ferrous sulphide is of similar variable composition.

Ferrous sulphide when pure is a yellowish crystalline mass with a metallic lustre, m. pt. 1170° ; the commercial substance is black or dark grey and contains free iron. It dissolves readily in dilute acids and is used in the preparation of hydrogen sulphide. A greenish-black precipitate of ferrous sulphide is formed when ammonium sulphide is added to a solution of a ferrous salt, or hydrogen sulphide passed into ferrous

sulphate solution containing sodium acetate. The precipitate dissolves slightly in excess of yellow ammonium sulphide forming a dark greenish-black solution, perhaps containing a thioferrite NH_4FeS_2 .

Ferric sulphide Fe_2S_3 is formed by the action of hydrogen sulphide on pure moist ferric hydroxide in absence of oxygen, and as a black precipitate by the action of excess of ammonia and ammonium sulphide on a solution of a ferric salt; with excess of ferric salt a mixture of FeS and sulphur is formed.

Thioferrites $\text{M}^{\text{I}}\text{Fe}^{\text{III}}\text{S}_2$ are formed by the action of alkali sulphides on ferric sulphide: $\text{K}_2\text{S} + \text{Fe}_2\text{S}_3 = 2\text{KFeS}_2$, or alkali polysulphides on ferrous sulphide: $(\text{NH}_4)_2\text{S}_2 + 2\text{FeS} = 2\text{NH}_4\text{FeS}_2$. Potassium thioferrite KFeS_2 is formed in insoluble purple needles on fusing iron filings, potassium carbonate, and sulphur, and extracting the fused mass with water. On heating it forms $\text{K}_2\text{Fe}_2^{\text{II}}\text{S}_3$. It evolves hydrogen sulphide and deposits sulphur with acids: $2\text{KFeS}_2 + 6\text{HCl} = 2\text{KCl} + 2\text{FeCl}_2 + 3\text{H}_2\text{S} + \text{S}$. The sodium salt $\text{NaFeS}_2 \cdot 2\text{H}_2\text{O}$ is also insoluble.

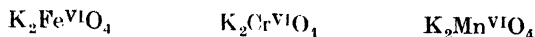
Iron disulphide FeS_2 occurs as *iron pyrites* and *marcasite*. Pyrites is stable in air, marcasite oxidises in moist air to ferrous sulphate. Pyrites crystallises in the regular system, often in plain or striated cubes (over 200 forms have been described). It has a brassy-yellow colour ("fool's gold"), is very hard, striking sparks from steel, and is not magnetic. Marcasite occurs in rhombic crystals, usually in the form of radiating nodules and is pale-yellow or white like tin. Pyrites often occurs in coal and is the source of much of the sulphur dioxide formed on its combustion. It is found in masses having the form of wood, roots, etc., and probably formed by reduction of solutions of ferrous sulphate by organic matter. Pyrites on heating in absence of air loses some sulphur and if heated in air, all the sulphur is burnt to dioxide (p. 463).

Pyrites is insoluble in dilute acids but readily dissolves in concentrated nitric acid (with separation of sulphur) and in aqua regia. Artificial FeS_2 is formed by heating ferrous sulphide with sulphur, by passing hydrogen sulphide over iron oxides or chlorides heated to redness, or by heating a mixture of ferric oxide, ammonium chloride and sulphur. FeS_2 contains *ferrous* iron and is a derivative of H_2S_2 .

The crystal lattices of pyrites and marcasite contain S_2 groups in which the atoms are linked by covalent bonds. The centres of these and the iron atoms occupy the positions of the sodium and chloride ions in the rock-salt lattice (p. 389), each iron atom being at the centre of an octahedral group of six sulphur atoms. In the pyrites lattice the axes of the $-\text{S}-\text{S}-$ groups are parallel to the four trigonal symmetry axes (p. 351) passing through diagonally opposite corners of the cube (the digonal and tetragonal symmetry axes have disappeared). The marcasite lattice is somewhat less symmetrical than the pyrites lattice.

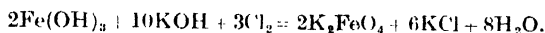
FERRATES

Ferrates (sometimes called *perferrates*) are compounds of the unknown iron trioxide FeO_3 containing 6-valent iron, and correspond with chromates and manganates :



and K_2FeO_4 is isomorphous with K_2SO_4 , K_2CrO_4 , K_2MnO_4 and K_2MoO_4 .

A mixture of one part of iron filings and two parts of nitre deflagrates on heating, and the cold product dissolves in water to form a purple solution (Stahl, 1703). This contains potassium ferrate K_2FeO_4 (Fremy, 1841). The purple solution is also formed by the electrolysis of potassium hydroxide solution with a cast-iron anode, or by passing chlorine into a suspension of ferric hydroxide in potassium hydroxide solution :



On adding solid potassium hydroxide to the solution, reddish-brown potassium ferrate K_2FeO_4 , is deposited. On boiling, a yellow solution of potassium ferrite (sometimes called ferrate) $\text{K}_2\text{Fe}_2\text{O}_4$, is formed, which rapidly deposits ferric hydroxide. On addition of barium chloride to the red potassium ferrate solution, fairly stable barium ferrate $\text{BaFeO}_4 \cdot \text{H}_2\text{O}$ is formed as a red precipitate.

A green *perferrate* K_2FeO_5 (derived from FeO_4) is said to be formed on fusing ferric oxide with potassium hydroxide and *excess* of potassium nitrate or chlorate.

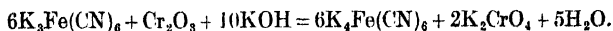
CYANOGEN COMPOUNDS OF IRON

Potassium ferrocyanide.—When nitrogenous organic matter such as horn or leather-clippings is fused with potassium carbonate and iron filings and the mass digested with water, the solution on evaporation deposits yellow crystals of potassium ferrocyanide (*yellow prussiate of potash*) $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. A ferric salt gives with the solution a deep-blue precipitate of *Prussian blue*, the first ferrocyanogen compound to be discovered (Diesbach, 1704). Macquer (1752) showed that potassium ferrocyanide is formed on boiling Prussian blue with potash, and Porret (1814) that **hydroferrocyanic acid** $\text{H}_4\text{Fe}(\text{CN})_6$ is formed as a white precipitate on adding an acid and then ether, to a solution of ferrocyanide. The precipitate contains combined ether. Berzelius pointed out that the yellow prussiate might be regarded as a double cyanide of potassium and ferrous iron, $4\text{KCN} \cdot \text{Fe}(\text{CN})_2$, but it is now regarded as the potassium salt of hydroferrocyanic acid, $\text{K}_4[\text{Fe}(\text{CN})_6]$. One of the CN groups may be replaced by CO, H_2O , NO, NO_2 , SO_3 , etc.

Potassium ferrocyanide is prepared from the spent-oxide of gas works (p. 613). The nitrogen of the coal is partly evolved as hydrocyanic acid, which collects in the oxide purifiers as Prussian blue. The spent oxide is heated with milk of lime, forming calcium ferrocyanide, and on adding potassium chloride $\text{K}_2\text{CaFe}(\text{CN})_6$ is precipitated: this is decomposed by adding potassium carbonate. Ferrocyanide is formed by adding excess of potassium cyanide to a solution of ferrous sulphate, until the brown pre-

precipitate redissolves. The crystals are yellow tetragonal pyramids, which are unchanged in air but on heating fall to a white powder of anhydrous salt. Potassium ferrocyanide, it is said, is not poisonous. The sodium salt $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ is prepared in a similar manner. Silver nitrate gives a white precipitate of silver ferrocyanide $\text{Ag}_4\text{Fe}(\text{CN})_6$ with soluble ferrocyanides.

Potassium ferricyanide.—When chlorine is passed into a solution of potassium ferrocyanide the ferrocyanide ion is *oxidised* to the ferricyanide ion, the two ions containing bi- and ter-valent iron respectively: $2\text{Fe}(\text{CN})_6^{4-} + \text{Cl}_2 = 2\text{Fe}(\text{CN})_6^{3-} + 2\text{Cl}^-$. At the same time a molecule of chlorine is *reduced* to two chloride ions. The two salts KCl and $\text{K}_3\text{Fe}(\text{CN})_6$ separate on evaporation from the yellowish-brown solution, but by repeated recrystallisation potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ is obtained pure in the form of anhydrous dark-red monoclinic prisms (*red prussiate of potash*, L. Gmelin, 1822). It is an oxidising agent, converting lithium into lead dioxide and chromic oxide into potassium chromate in boiling alkaline solution:



The solution is reduced to ferrocyanide by sodium amalgam or glucose in alkaline solution. The alkaline solution is reduced by hydrogen peroxide; acid solution of ferrocyanide is oxidised by the same reagent (p. 196). **Sodium ferricyanide** $2\text{Na}_3\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$ is obtained from sodium ferrocyanide and chlorine.

Hydroferricyanic acid $\text{H}_3\text{Fe}(\text{CN})_6$ is formed in brown needles by decomposing lead ferricyanide with dilute sulphuric acid, filtering and evaporating.

Lead ferricyanide $\text{Pb}_3[\text{Fe}(\text{CN})_6]_2 \cdot 16\text{H}_2\text{O}$ is formed in brown crystals on mixing hot solutions of lead nitrate and potassium ferricyanide.

Silver ferricyanide $\text{Ag}_3\text{Fe}(\text{CN})_6$ is formed as a red precipitate on adding silver nitrate to potassium ferricyanide solution.

Prussian blue.—When a solution of ferrous sulphate is added to a cold *neutral* solution of potassium ferrocyanide, a white precipitate of **potassium ferrous ferrocyanide** $\text{K}_2\text{Fe}''(\text{Fe}''\text{Cy}_6)$ is formed*, which rapidly oxidises in air to β -soluble **Prussian blue** or potassium ferric ferrocyanide $\text{Fe}'''\text{K}(\text{Fe}'''\text{Cy}_6) \cdot \text{H}_2\text{O}$, insoluble in oxalic acid but soluble in water. But with *acid* ferrocyanide solution the white precipitate formed is less readily oxidised and on exposure to air forms γ -soluble **Prussian blue**, probably with the same formula as the β -blue but more stable to alkalis, acids and ferric chloride.

When potassium ferrocyanide is boiled with dilute sulphuric acid, hydrocyanic acid is evolved: $2\text{K}_4\text{FeCy}_6 + 3\text{H}_2\text{SO}_4 = 3\text{K}_2\text{SO}_4 + \text{K}_2\text{Fe}''(\text{Fe}''\text{Cy}_6) + 6\text{HCN}$. The pale-yellow powder, $\text{K}_2\text{Fe}(\text{FeCy}_6)$, also formed, is much less easily oxidised than the other two forms described, but nitric acid or hydrogen peroxide converts it into **Williamson's violet**, $\text{KFc}''(\text{Fe}''\text{Cy}_6) \cdot \text{H}_2\text{O}$.

By heating a solution of hydroferrocyanic acid at 110° – 120° in a sealed tube a precipitate of the acid corresponding with the white precipitates, $\text{H}_2\text{Fe}''(\text{Fe}''\text{Cy}_6)$ is formed, which on oxidation gives a violet compound, possibly $\text{HF}''(\text{Fe}''\text{Cy}_6)$.

When a solution of potassium ferrocyanide is precipitated with rather less than the equivalent of ferric chloride and the precipitate washed by

* In this section the cyanogen radical CN is denoted by Cy, and the valency of the iron by dashes.

decantation with potassium chloride solution, then with 70 per cent alcohol, and dried over P_2O_5 , it forms α -soluble Prussian blue or α -ferric potassium ferrocyanide, $4Fe'''K(Fe''C_6), 7H_2O$. This when dried has a bronze lustre and forms a beautiful deep-blue powder. It dissolves in water forming a blue colloidal solution, and is soluble in oxalic acid.

α -soluble Prussian blue may have the formula $Fe'''K(Fe''C_6)$ or $Fe''K(Fe'''C_6)$. K. A. Hofmann (1904) showed that hydrogen peroxide in acid solution (which reduces ferricyanides to ferrocyanides) reduces ferric ferricyanide solution but oxidises ferrous ferrocyanides to Prussian blue, and the latter must therefore contain the ferric iron in the basic radical. The same Prussian blue is formed by precipitating a ferricyanide with a ferrous salt, and in this case, isomeric change must have occurred.

With excess of ferric chloride, the precipitate becomes insoluble in water and is called insoluble Prussian blue: it has the formula $Fe'''_4(Fe''C_6)_3$ or Fe_7C_6 , but contains water which cannot be driven off by heat, and is generally formulated as $Fe_7C_6 \cdot 9H_2O$. It is the main constituent of ordinary Prussian blue.

The precipitate obtained by adding an excess of ferrous salt to potassium ferricyanide, known as Turnbull's blue, was formerly considered to be ferrous ferricyanide $Fe_3''(Fe'''C_6)_2$ but it is identical with insoluble Prussian blue. A ferric salt with potassium ferrocyanide gives a deep-brown solution, probably containing ferric ferricyanide, but no precipitate. A little stannous chloride or granulated zinc and acid, added to the solution, precipitates Prussian blue. If chlorine is passed into a boiling solution of potassium ferrocyanide in the dark, a green precipitate called Berlin green, probably polymerised ferric ferricyanide $Fe'''(Fe''C_6)$, is formed.

(The above account is based on the researches of K. A. Hofmann; other formulae have been proposed).

The structures of soluble Prussian blue, potassium ferrous ferrocyanide, and Berlin green as found by the X-rays (Keggin and Miles, 1936) are shown in Fig. 391. The lattice of soluble Prussian blue or $KFe'''[Fe''(CN)_6]$ is

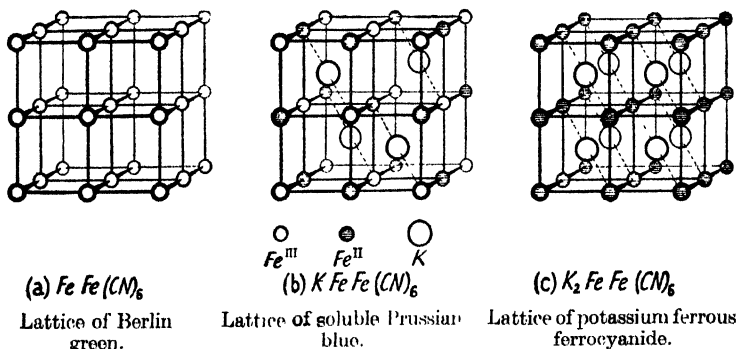


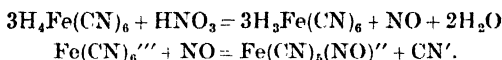
FIG. 391.

From Wells: *Structural Inorganic Chemistry* (Clarendon Press)

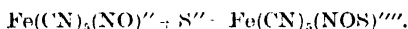
cubic with ferrous and ferric atoms alternately at the corners and CN radicals on the edges, the K atoms being shown at the centres of alternate

small cubes. Potassium ferrous ferrocyanide $K_2Fe''[Fe''(CN)_6]$ has a similar structure, but all the iron atoms are ferrous and to balance the charges a potassium atom is at the centre of every cube. In Berlin green all the iron atoms are ferric and there are no alkali metal atoms in the lattice. Ruthenium purple $KFe'''[Ru''(CN)_6]$ has a similar structure to soluble Prussian blue $KFe'''[Fe''(CN)_6]$.

Sodium nitroprusside.—Potassium ferrocyanide warmed with 50 per cent. nitric acid gives a brown solution. When a slate-coloured precipitate is formed with ferrous sulphate the liquid is cooled, separated from the crystals of potassium nitrate, and neutralised with sodium carbonate. The filtered solution on evaporation gives red rhombic crystals of **sodium nitroprusside** (Playfair, 1849), $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$, which may be freed from nitrate by repeated crystallisation. A nitroprusside is formed on passing NO into acidified ferricyanide solution :



A freshly-prepared solution of sodium nitroprusside (it decomposes on standing) gives with alkali sulphides (but not with free hydrogen sulphide) an intense purple colour (Gmelin, 1848, with crude nitroprusside solution), perhaps due to $[Fe(O:N:S)(CN)_5]''''$:



With alkali sulphite a nitroprusside gives a rose-red colour (Boedeker, 1861) and a pale-yellow salt with the formula $Na_5[Fe(CN)_5SO_3] \cdot 9H_2O$ is formed.

Silver nitrate gives with sodium nitroprusside a flesh-coloured precipitate of $Ag_2[Fe(CN)_5(NO)]$ and by reaction of this with hydrochloric acid the unstable free acid $H_2[Fe(NO)(CN)_5]$ is formed.

The nitroprussides were usually considered to contain ferric iron and the neutral NO molecule, $Fe^{III}(C_5N_5NO)$ giving the valency $3 - 5 - 2$, but Pauling (1931) suggested that the odd electron of the NO molecule $\cdot : N : : O :$ enters the valency shell of the ferric ion in $K_3Fe(C_5N_5NO)$, forming a *ferrous* ion, and the $\cdot : N : : O :$ radical then coordinates by the electron pair on the nitrogen. This gives the valency $2 - 5 + 1 = -2$, since the (NO) has now become positively univalent.

Ferric thiocyanate is formed when potassium or ammonium thiocyanate is added to a solution of a ferric salt. It has a deep blood-red colour, and its formation is a delicate test for the ferric ion. The reaction is reversible : $FeCl_3 + 3KCN \rightleftharpoons Fe(CNS)_3 + 3KCl$. If the solution is shaken with ether, this dissolves the ferric thiocyanate. Mercuric chloride discharges the red colour of the aqueous solution ; the mercury salt, which is only slightly ionised, is formed from the ferric salt. Reducing agents form ferrous thiocyanate, colourless in solution. The red colour has also been supposed to be due to a complex ion $Fe(CNS)_6'''$ or $Fe(CNS)''$.

Roussin's salts.—If a solution of ferrous sulphate in excess of a thio-sulphate is saturated with nitric oxide, a crystalline **iron dinitrosothiosulphate** is formed, e.g. reddish-brown leaflets of $K[Fe(NO)_2S_2O_3] \cdot H_2O$, or brilliant jet-black crystals of $Rb[Fe(NO)_2S_2O_3] \cdot H_2O$. If nitric oxide is passed into a suspension of precipitated ferrous sulphide in dilute solutions of alkali

sulphides, or ferrous sulphate acts on a mixture of alkali, nitrite and sulphide, *black Roussin's salts* are formed, *e.g.* $\text{KFe}_4(\text{NO})_7\text{S}_3$, which form dark-brown solutions with water. By the action of boiling alkalis on these, *red Roussin's salts* such as $\text{KFe}(\text{NO})_2\text{S}$ are formed.

The atomic weight of iron has been determined by the reduction of ferric oxide (from carefully purified ferric nitrate) in hydrogen ; this is one of the very rare cases in which the analysis of an oxide has been used in an accurate atomic weight determination. Another method used was the determination of the ratio $\text{FeBr}_2 : 2\text{AgBr}$. The valency is found from the atomic heat and the vapour densities of ferric chloride (p. 931) and iron carbonyl $\text{Fe}(\text{CoO})_5$.

CHAPTER XLVII

GROUP VIII METALS: COBALT AND NICKEL

COBALT

Historical.—The use of cobalt as a constituent of some blue glazes and blue glass made in imitation of lapis lazuli is established for ancient Egypt (1375 B.C.) and ancient Babylonia (about 1450 B.C.) by analysis of actual specimens. Most ancient blue glazes, however, owe their colour to a compound of copper, $\text{CuO}, \text{CaO}, 4\text{SiO}_2$. Some specimens of Roman blue glass (e.g. a piece found at Uriconium) are coloured with cobalt.

The name *cobalt* is used by Agricola and other German writers for certain minerals which resembled ores of metals, yet did not yield metal with the usual treatment but gave off an arsenical smell. The roasted *cobalt*, called *zaffre* (impure cobalt arsenate), gives on fusion with sand and potassium carbonate a beautiful blue glass called *smalt*. The blue colour, at first believed to be due to arsenic, was shown by Brandt (1735) to come from a new metal and Bergman (1780) investigated its properties.

Occurrence.—The arsenide of cobalt, nickel and iron $(\text{Co}, \text{Ni}, \text{Fe})\text{As}_2$ (in the pure state CoAs_2) is known as *speiss cobalt* or *smaltite*. Cobalt is also found as *linnaeite* $(\text{Co}, \text{Ni}, \text{Fe})_3\text{S}_4$, *cobalt glance* or *cobaltite* $(\text{Co}, \text{Fe})\text{AsS}$, and as *erythrite* or *cobalt bloom* $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, but is now mostly obtained from arsenides and sulphides in the silver ores of Cobalt City, Ontario, and from the copper ores of Rhodesia and Katanga. Some is extracted from the cobalt glance of Queensland, and from New Caledonia manganese ore containing about 2 per cent of cobalt oxide. Cobalt is nearly always associated with nickel.

Metallurgy.—Metallic cobalt is obtained as a grey powder by strongly heating the oxide in hydrogen.

The details of the metallurgy of cobalt are rather complicated. The ore is roasted to free it from some arsenic and sulphur, and fused in a blast-furnace with limestone and sand as a flux. The iron passes into the slag and impure arsenide and antimonide of nickel and cobalt (*speiss*) settles out. This is ground, roasted to drive off most of the arsenic (and antimony, if present), and then roasted with salt. If silver is present it is extracted by cyanide. The residue is boiled with concentrated sulphuric acid and the "sulphated speiss" agitated with water; the iron, arsenic and antimony are precipitated with limestone, copper from the filtrate by sodium carbonate, and the cobalt by sodium hypochlorite, which precipitates cobalt peroxide. Finally, nickel is precipitated from the filtrate as basic carbonate by adding sodium carbonate, the last portions being thrown out as peroxide by adding a little hypochlorite.

The cobalt and nickel oxides are sold as such, or reduced by heating in an electric furnace with carbon and limestone. The metal usually contains about 1 per cent of carbon and 0.015 per cent of sulphur. The calcined cobalt oxide contains less than 1 per cent of nickel and 71–75 per cent of cobalt. The metal may also be prepared by the electrolysis of a solution of the sulphate, CoSO_4 , containing ammonium sulphate and ammonia.

In the preparation of very pure cobalt compounds, the cobalt is precipitated as the cobaltamine $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, a last trace of nickel being precipitated with dimethylglyoxime.

Properties.—Cobalt is tenacious, silver-white with a slight bluish cast which nickel has not, is readily polished and shows a high lustre. Its density is 8.8; it is magnetic up to 1100° , and melts at 1478° . Cobalt does not oxidise in air at atmospheric temperature and is harder and brighter than nickel; it was used for plating, but is now replaced by chromium. Cobalt slowly oxidises on heating in air. It absorbs 59–153 volumes of hydrogen when finely-divided. The metal dissolves slowly in dilute sulphuric acid and concentrated hydrochloric acid, but readily in nitric acid. It can become passive in cooled fuming nitric acid.

Cobalt steel (35 per cent Co) was used for permanent magnets for magnetos, as these can be made much smaller than carbon steel magnets, retain their magnetism much more tenaciously and do not tend to become demagnetised. A nickel-aluminium steel with more than twice the magnetic coercivity of cobalt steel is now used. *Stellite* is an alloy of chromium, tungsten and cobalt, very hard and non-corroding, used for surgical instruments. *Festel metal* is an alloy of cobalt, iron and chromium used for cutlery or electric heating elements.

Cobaltous compounds.—Cobalt in its compounds has valencies of 1, 2, 3, and (in impure CoO_2) 4. The commonest compounds are the cobaltous compounds of bivalent cobalt.

Univalent cobalt occurs in a complex ion $\text{Co}(\text{CN})_x$ present in a brownish-green solution, evolving hydrogen at room temperature, formed by reducing a solution of $\text{K}_3\text{Co}(\text{CN})_6$ with potassium amalgam.

Cobaltous chloride CoCl_2 sublimes in blue crystals, isomorphous with cadmium chloride, when cobalt is heated in chlorine, and is formed as a blue mass by heating any of the hydrates at 140° . The common hydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is formed in dark-red deliquescent crystals from a solution of cobalt or the oxide or carbonate in hydrochloric acid. The lower hydrates with 2 and $1\text{H}_2\text{O}$ are violet. The pink solution of cobaltous chloride becomes blue on heating above 50° or on adding concentrated sulphuric acid, and the solid hydrate gives a bluish-purple solution with alcohol. (Cobaltous nitrate solution becomes blue with concentrated hydrochloric acid but not with concentrated sulphuric acid).

A solution of cobalt chloride is a *sympathetic ink*, introduced about 1705; the writing is almost invisible but becomes blue on warming the paper before a fire. On standing in moist air the colour disappears.

The old theory that the colour changes are due to different degrees of hydration has been revived in a modified form, but the usually accepted view is that the blue colour in solutions is due to complex anions: $2\text{CoCl}_2 \rightleftharpoons \text{Co}^{++} + \text{CoCl}_4^{--}$. The CoCl_4^{--} ion was shown to migrate to the anode on electrolysis. The salt Cs_3CoCl_5 contains Cs^+ , Cl^- and CoCl_4^{--} (tetrahedral) ions (Powell and Wells, 1935).

Cobaltous bromide CoBr_2 , obtained by adding bromine to cobalt powder in ether and heating the $\text{CoBr}_2 \cdot \text{Et}_2\text{O}$ formed, is dark green; it forms hydrates with 6 (dark-red), 5 (violet-red) and 2 (purple) H_2O . **Cobaltous iodide** CoI_2 , which is black, obtained by heating cobalt in iodine vapour, and the hydrates with 9 (light-red), 6 (dark-red), and 2 (green) H_2O , are very deliquescent.

Cobaltous fluoride CoF_2 , formed by heating CoCl_2 in a current of HF , and the hydrate $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ are red (*cf.* CoCl_2).

Cobaltous oxide CoO , an olive-green powder and octahedral crystals, is formed by heating the hydroxide, by passing steam over red-hot cobalt: $\text{Co} + \text{H}_2\text{O} \rightleftharpoons \text{CoO} + \text{H}_2$ (*cf.* Fe and Ni), and by *strongly* heating the carbonate or nitrate out of contact with air. It is stable at 1000° , but when heated in air forms cobalto-cobaltic oxide Co_3O_4 . It dissolves in acids to form cobaltous salts, and with magnesium, zinc and aluminium oxides forms pink, green and blue cobaltites respectively.

A solution of cobalt nitrate is used in blowpipe analysis. The ignited residue on charcoal is moistened with one drop of dilute cobalt nitrate and reheated. Zinc gives a green mass (*Rinnman's green*, a solid solution), aluminium a blue mass (*Thenard's blue*, $\text{Al}_2(\text{CoO}_4)$), although blue masses are also produced with phosphates. Magnesia gives a pink mass, a solid solution. The compounds $4\text{CoO} \cdot 3\text{Al}_2\text{O}_3$, Co_2SnO_4 and CoCr_2O_4 are green. Cobalt salts give a beautiful blue borax bead. Cobalt chloride gives an evanescent red flame coloration.

Cobaltous hydroxide $\text{Co}(\text{OH})_2$ precipitated by alkali hydroxide from a cobaltous salt solution is first bluish-violet, but forms a pink powder on standing in presence of excess of alkali, more rapidly on boiling. The blue and pink varieties are different crystalline forms, the pink having a brucite $\text{Mg}(\text{OH})_2$ lattice. The moist hydroxide absorbs oxygen from air and forms brown Co_3O_4 . It dissolves in hot concentrated potassium hydroxide and separates on cooling as a violet crystalline powder.

Cobaltous carbonate CoCO_3 is rhombohedral and isomorphous with calcite. The hydrate $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$ is formed on standing as a pink precipitate from a cold solution of a cobaltous salt and sodium bicarbonate saturated with carbon dioxide; the precipitates with alkali carbonate or bicarbonate contain cobaltous hydroxide. Cobalt carbonate forms pink $\text{K}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ and bright reddish-purple $\text{Na}_2\text{Co}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$.

Cobaltous nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is formed in pink slightly deliquescent monoclinic crystals from a solution of the metal, oxide or

carbonate in dilute nitric acid. There are also hydrates with 9 and $3\text{H}_2\text{O}$. The slightly pink anhydrous salt is formed (Guntz and Martin, 1909) by the action of concentrated nitric acid and N_2O_5 on the hexahydrate (which decomposes on heating to form Co_3O_4).

Cobaltous sulphide CoS is formed as a black precipitate by ammonium sulphide, or hydrogen sulphide in presence of sodium acetate. Although not precipitated by hydrogen sulphide from acid solutions, it is insoluble in dilute acids but soluble in concentrated hydrochloric acid and aqua regia. Precipitated cobalt and nickel sulphides are apparently the hydrosulphides $\text{Co}(\text{SH})_2$ and $\text{Ni}(\text{SH})_2$, which absorb oxygen on exposure to air and form sulphates (Middleton and Ward, 1935).

Cobalt disulphide CoS_2 precipitated by yellow ammonium sulphide from a cobaltous solution, or formed by heating CoS and sulphur, contains *bivalent cobalt* (De Jong and Williams, 1927).

Cobaltous sulphate CoSO_4 , obtained anhydrous by heating a hydrate at 250° , boiling it with concentrated sulphuric acid, or heating it with ammonium sulphate, is a pale-reddish or lavender-coloured powder, consisting of small rhombic crystals. All the hydrates are pink or red. The common hydrate, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, crystallises below 44° from solutions of cobalt, the oxide or carbonate in dilute sulphuric acid; it is monoclinic, isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and efflorescent, m. pt. 97° . Between 44° and 70° monoclinic $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ isomorphous with $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ crystallises, and above 70° $\text{CoSO}_4 \cdot \text{H}_2\text{O}$, the solubility of which decreases with rise in temperature. When poured into concentrated sulphuric acid, a solution precipitates as $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$.

Red double sulphates $\text{M}'_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($\text{M}' = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Th}$) are readily formed: they belong to the schonite group (p. 776) and are all monoclinic and isomorphous (also with corresponding compounds with bivalent $\text{Ni}, \text{Fe}, \text{Zn}, \text{Cd}, \text{Mg}$, etc.).

Ammonium thiocyanate gives with a cobaltous salt solution (especially in presence of acetone) a deep-blue colour due to $\text{Co}(\text{CNS})_4^{2-}$, extracted by ether or amyl alcohol: from the aqueous solution a blue salt $(\text{NH}_4)_2[\text{Co}(\text{CNS})_4]$ can be crystallised. A mercuric salt and a thiocyanate with a cobaltous solution form a deep-blue crystalline precipitate of $\text{Co}[\text{Hg}(\text{CNS})_4]$.

Cobaltic compounds.—There is much confusion about the higher oxides of cobalt. The dark-brown or black powder formed on heating cobalt nitrate (sometimes described as Co_2O_3) is **cobalto-cobaltic oxide** Co_3O_4 , octahedral, with a spinel structure, $\text{Co}^{\text{II}}(\text{Co}^{\text{III}}\text{O}_2)_2$, also formed by heating CoO or Co_2O_3 at 600° – 700° in air. Unlike Fe_3O_4 it is non-magnetic. The black precipitate from cobalt solutions by hypochlorite, alkali and iodine, hydrogen peroxide or ammonium persulphate is hydrated **cobaltic oxide** Co_2O_3 , although some **dioxide** $\text{Co}^{\text{IV}}\text{O}_2$ is formed by adding a further quantity of hypochlorite.

Definite hydrates of Co_2O_3 with 1, 2 and $\frac{5}{2}\text{H}_2\text{O}$ are claimed from breaks in the dehydration curve. Cobaltates, e.g. crystalline $\text{BaCo}^{\text{IV}}\text{O}_3$, derived from $\text{Co}^{\text{IV}}\text{O}_2$, are described (*percobaltites*, e.g. Co_3O_4 or $\text{Co}(\text{CoO}_2)_2$, are derived from Co_2O_3).

Another cobaltic compound is **cobaltic fluoride** CoF_3 , a green solid formed by the action of fluorine on CoCl_2 at 150° ; a green hydrate $2\text{CoF}_3 \cdot 7\text{H}_2\text{O}$, decomposed by water, is formed by electrolytic oxidation of a solution of CoF_2 in 40 per cent hydrofluoric acid (Barbieri, 1905-28; Ruff and Ascher, 1929). Blue **cobaltic cyanide** $\text{Co}(\text{CN})_3$ and red $\text{Co}(\text{CN})_3 \cdot 2\text{H}_2\text{O}$ (Rây, 1933-4), and **cobaltic sulphide** Co_2S_3 formed from the elements at 350° - 400° , are known.

Cobaltic sulphate $\text{Co}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ is deposited in silky blue needles by electrolytic oxidation of a cooled saturated solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in 40 per cent sulphuric acid: it forms blue **cobaltic alums** $\text{MCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) which (like the sulphate) are rather unstable, evolving ozonised oxygen in solution (Marshall, 1891). All simple cobaltic salts are powerful oxidising agents.

When hydrogen peroxide is added to a suspension of cobaltous hydroxide the filtrate is acid and gives a green colour with KHCO_3 . It has been supposed to contain cobaltic acid H_2CoO_3 , or a complex cobaltic compound $[\text{Co}(\text{KCO}_3)_2]_2\text{O}$, or a compound $\text{CoCO}_3 \cdot \text{Co}_2\text{O}_3$, or a complex cobaltic carbonate $\text{Co}[\text{Co}(\text{CO}_3)_3]$.

Complex cobaltic compounds.—The commonest cobaltic compounds are complex, the most important being the cobaltamines, the cobaltinitrites and the cobaltcyanides.

Precipitated cobaltous hydroxide dissolves in excess of ammonia to a yellowish-brown solution which deposits cobaltous hydroxide on dilution. On exposure to air the solution absorbs oxygen, more rapidly on boiling or heating with lead dioxide, and forms a pink solution of a **cobaltamine**. More than 2000 compounds of this type are known. The following are typical:

(i) A solution of ammonium carbonate and ammonia is added to cobalt nitrate solution and air is drawn through the violet liquid; oxidation occurs and a blood-red solution of the compound *tetrammine-carbonato-cobaltic nitrate* $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ is formed, which gives purple crystals (with $\frac{1}{2}\text{H}_2\text{O}$) on evaporation.

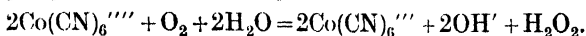
(ii) On acidifying a solution of this with hydrochloric acid, heating with excess of ammonia, and adding concentrated hydrochloric acid, *pentammine-chloro-cobaltic dichloride* $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is formed.

(iii) On heating $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ with ammonium chloride and ammonia in a pressure bottle, adding hydrochloric acid and cooling, *hexammine-cobaltic trichloride* $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is formed.

(iv) From a solution of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in ammonia, cooled in ice, slow addition of concentrated hydrochloric acid precipitates *aquo-pentammine-cobaltic trichloride* $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$.

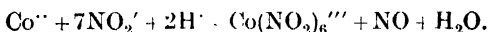
Cobaltcyanides contain the very stable complex anion $\text{Co}(\text{CN})_6^{4-}$ containing 3-valent cobalt. Potassium cyanide gives with a cobalt salt

solution a reddish-brown precipitate of cobaltous cyanide $\text{Co}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$, soluble in excess to a yellow solution of potassium cobaltocyanide $\text{K}_4\text{Co}(\text{CN})_6$, containing 2-valent cobalt and analogous to ferrocyanide; this is precipitated as an amethyst-coloured powder by alcohol. On adding a little acetic or hydrochloric acid to the cobaltocyanide solution and boiling in a dish for a few minutes, oxidation occurs and potassium cobalticyanide $\text{K}_3\text{Co}(\text{CN})_6$, containing 3-valent cobalt and analogous to ferricyanide, is formed (Gmelin, 1827), and an equivalent amount of hydrogen peroxide is formed by autoxidation:



Potassium cobalticyanide forms stable yellow crystals isomorphous with the ferricyanide. With silver nitrate it gives a white precipitate of silver cobalticyanide $\text{Ag}_3\text{Co}(\text{CN})_6$ and with copper sulphate a blue precipitate of cupric cobalticyanide $(\text{Cu}_3[\text{Co}(\text{CN})_6]_2)$, from which by precipitation of the copper by hydrogen sulphide colourless crystalline hydrocobalticyanic acid $\text{H}_3\text{Co}(\text{CN})_6$ is formed. Cobalticyanides give no reactions of cobalt or cyanides and are not decomposed by concentrated nitric acid or hypochlorite.

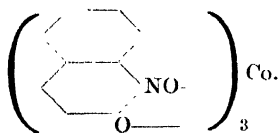
Cobaltinitrites contain the complex anion $\text{Co}(\text{NO}_2)_6'''$ containing 3-valent cobalt. Potassium nitrite gives with a cobaltous salt solution acidified with acetic acid a yellow precipitate of potassium cobaltinitrite $\text{K}_3\text{Co}(\text{NO}_2)_6$ (*Fischer's salt*), sparingly soluble in water:



This is formed only in acid solutions, otherwise the cobaltinitrite $\text{K}_2\text{Co}(\text{NO}_2)_4$, containing 2-valent cobalt, is produced. The cobaltinitrite is less stable than the cobalticyanide and is decomposed by ammonium sulphide. It is used as a yellow pigment (*Indian, or cobalt, yellow*) and in painting porcelain blue.

A reagent for potassium is prepared by dissolving 30 gm. of cobalt nitrate and 50 gm. of sodium nitrite in 150 ml. of water and adding 10 ml. of glacial acetic acid. The addition of silver nitrate makes it more sensitive, as the salts $\text{K}_2\text{AgCo}(\text{NO}_2)_6$ and $\text{KAg}_2\text{Co}(\text{NO}_2)_6$ are less soluble than $\text{K}_3\text{Co}(\text{NO}_2)_6$; 1 part of potassium in 10,000 of water may be detected.

A compound of tervalent cobalt is cobalti- α -nitroso- β -naphthol, formed as a brownish-red precipitate on warming a solution of a cobaltous salt with a solution of α -nitroso- β -naphthol in acetic acid. Nickel is not precipitated.



If the Co^{II} is converted into Co^{III} by precipitating cobaltic hydroxide by alkali and H_2O_2 and dissolving this in acetic acid, precipitation of $\text{Co}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3 \cdot 2\text{H}_2\text{O}$ is quantitative.

NICKEL

History.—A coin of the Bactrian king Euthydemus (235 B.C.) contains 77.58 per cent of copper and 20.04 per cent of nickel, and alloys of copper, zinc and nickel seem to have been used in China before this date. The German miners obtained a mineral resembling copper ore from which no metal could be extracted, and to this the name *kupfer-nickel* (i.e. "false-copper") was given by Hiärne (1694). In 1751 Cronstedt obtained impure metallic nickel from this ore and the properties of nickel were investigated more thoroughly by Bergman in 1774.

Occurrence.—The chief ores of nickel are the cobalt ore *smaltite* $(\text{Ni}, \text{Co}, \text{Fe})\text{As}_2$, *chloanthite* or *white nickel ore* NiAs_2 , *kupfer-nickel* or *niccolite* NiAs , *nickel glance* NiAsS , *millerite* NiS , *annabergite* or *nickel bloom* $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, and the important ores *garnierite* $(\text{Ni}, \text{Mg})\text{SiO}_3 \cdot x\text{H}_2\text{O}$ found in New Caledonia, and *pentlandite* $(\text{Fe}, \text{Ni})\text{S}$ containing about 22 per cent of nickel found at Sudbury, Ontario. Nickel is found in meteoric iron, and is also obtained as a by-product in electrolytic copper refining.

Metallurgy.—The Sudbury ores (the most important) contain pentlandite, *chalcopyrite* CuFeS_2 and *pyrrhotite* Fe_8S_9 , which are partly separated by flotation. The pentlandite with some chalcopyrite is roasted, smelted and bessemerised, yielding a *matte* containing copper, nickel and sulphur, with a little iron. This may be worked up to give *monel metal*, containing nickel and copper with some iron and manganese and resembling nickel in colour and properties.

If the *matte* is melted with coke and salteak (which form sodium sulphide) and poled, two strata separate (*Orford process*). The upper layer contains sodium and cuprous sulphides, the lower layer nickel sulphide NiS . The lower layer is purified and is roasted to nickel oxide NiO , which is reduced by heating strongly with carbon.

Nickel is extracted from Canadian *matte* by the **Mond carbonyl process**, worked in South Wales. The roasted *matte* (still containing some sulphur) is leached with dilute sulphuric acid to remove copper, which is converted into blue vitriol. The residue is reduced at about 300° to 350° by water gas. Nickel oxide but not ferric oxide is reduced by hydrogen at this temperature. The mass is next passed at 60° down a tower provided with shelves and carbon monoxide is passed through, when volatile **nickel carbonyl** $\text{Ni}(\text{CO})_4$ is produced. The gas containing this is passed through a decomposer heated at 150° – 180° . Decomposition of the carbonyl occurs and metallic nickel is deposited on nickel pellets kept stirred, the carbon monoxide passing back to the volatiliser: $\text{Ni}(\text{CO})_4 \rightleftharpoons \text{Ni} + 4\text{CO}$. The nickel is 99.8 per cent pure: it contains 0.06 per cent of iron, 0.09 per cent of carbon, and traces of sulphur and silicon. Nickel may be cast (m.pt. 1452°); a little magnesium may be added before casting to increase the fluidity and remove gas bubbles.

Nickel is refined by electrolytic deposition from a solution of nickel ammonium sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at 20° – 25° , a cast nickel

block being used as anode and a thin polished sheet of pure nickel as cathode. The anode mud contains platinum metals (which are extracted). The same process is used in nickel-plating, a thin layer of copper being first deposited on iron or steel goods.

Metallic nickel is silver-white with a grey tinge, is hard and malleable and takes a high polish. It is magnetic below 340° . Nickel is fairly resistant to pure air but in town air containing acid and soot it rapidly tarnishes and acquires a green patina of basic sulphate, so that nickel-plating is now covered with chromium. The metal is resistant to fused alkalis and is used for crucibles; containers for milk have also been used. Nickel oxidises only very slowly when heated in air and decomposes steam only very slowly at a red heat: $\text{Ni} + \text{H}_2\text{O} = \text{NiO} + \text{H}_2$.

Finely-divided nickel absorbs 17 times its volume of hydrogen and acts as a catalyst in hydrogenation reactions, e.g. the absorption of hydrogen by liquid oils containing glycerol esters of unsaturated fatty acids. When treated with hydrogen at 150° to 250° in presence of finely-divided nickel these take up hydrogen and become solid fats. A black solid **nickel hydride** NiH_2 , also **cobalt hydride** CoH_2 and **iron hydrides** FeH_2 and FeH_3 , are described. They are formed by passing hydrogen into a solution of magnesium phenyl bromide in ether containing the corresponding chloride of the metal. Melted nickel at 2100° dissolves carbon, but this is deposited on solidification and no carbide is obtained (cf. Fe).

Nickel is used chiefly to make *nickel steel*, usually containing about 3.5 per cent of nickel, or nickel crucibles and tubes, and alloyed with 75 per cent of copper for coinage. An alloy of copper and nickel is used for coating rifle bullets. *Nichrom*, an alloy of nickel, iron and chromium, melts at a high temperature and is used for electric resistance heaters. *German silver* is an alloy of copper, nickel and zinc. A similar alloy has long been used in China under the name *paktong*.

NICKEL COMPOUNDS

Nickel dissolves in dilute nitric acid to a green solution. The colour is that of the nickel ion Ni^{2+} or $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and is shown by all simple salts of nickel. Nickel becomes passive in concentrated nitric acid. In its common compounds nickel is bivalent. It is trivalent in Ni_2O_3 and quadrivalent in NiO_2 .

Univalent nickel is present as $\text{KNi}(\text{CN})_2$ in the deep-red solution formed by heating $\text{K}_2\text{Ni}(\text{CN})_4$ solution with zinc, from which $\text{Ni}(\text{CN})_2$ is precipitated by acids. The compound $\text{K}_4\text{Ni}(\text{CN})_4$, prepared by the action of excess of potassium on $\text{K}_2\text{Ni}(\text{CN})_4$ in liquid ammonia, contains *zero-valent nickel* (Easton and Burgess, 1942).

Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is produced by dissolving the metal in aqua regia and evaporating. On heating, the deliquescent green crystals form yellow anhydrous NiCl_2 .

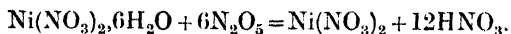
Alkali hydroxide gives with solutions of nickel salts an apple-green precipitate of **nickel hydroxide** $\text{Ni}(\text{OH})_2$, insoluble in excess but somewhat

soluble in ammonia and soluble in ammonium salts forming blue solutions, from which $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Ni}(\text{NH}_3)_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ may be obtained in blue crystals. On heating the hydroxide nickel monoxide NiO is obtained as a green mass; this is also formed on strongly heating the nitrate, but at a lower temperature a black sesquioxide Ni_2O_3 is formed, which liberates chlorine when dissolved in hydrochloric acid. The black precipitate formed by the action of chlorine or hypochlorite on a suspension of nickel hydroxide contains the hydrated dioxide NiO_2 and hydrated Ni_2O_3 . Nickel hydroxide is not oxidised by atmospheric oxygen or hydrogen peroxide.

A green hydrate of nickel peroxide $\text{NiO}_2 \cdot x\text{H}_2\text{O}$ is precipitated by adding cooled alcoholic potash to a strongly cooled mixture of nickel chloride and hydrogen peroxide; it forms hydrogen peroxide with acids. Nickel tetroxide NiO_4 is said to be formed by the electrolysis of a hot solution of a nickel salt containing chromic acid and alkali pyrophosphate.

Nickel carbonate $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ is obtained as a green precipitate by adding nickel sulphate to a solution of sodium bicarbonate saturated with carbon dioxide. The precipitate formed with sodium carbonate contains nickel hydroxide.

Nickel nitrate is formed in grass-green crystals $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on evaporating a solution of the metal or oxide in dilute nitric acid; it is very soluble in water. The anhydrous nitrate cannot be obtained by heating the hydrate, which decomposes (see above), but is formed by the action of fuming nitric acid and nitrogen pentoxide on the hydrate:

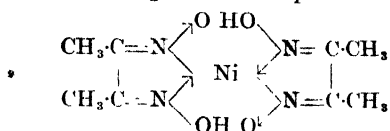


Nickel sulphide NiS is formed as a black precipitate when ammonium sulphide is added to a solution of a nickel salt. It dissolves slightly in excess of ammonium sulphide, forming a dark-brown solution from which it is precipitated by boiling, exposure to air, or addition of acids. Precipitated nickel sulphide easily oxidises when moist on exposure to air, unless precipitated by boiling a nickel salt solution with sodium thiosulphate, when it is much denser. It is insoluble in dilute acids (although it is not precipitated by hydrogen sulphide from acid solutions) but dissolves in warm aqua regia. It is supposed that three different forms of nickel sulphide are precipitated under different conditions (Thiel and Gessner, 1914).

Nickel sulphate is obtained in bright-green crystals $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ isomorphous with Epsom salt from solutions of nickel oxide or basic carbonate in dilute sulphuric acid. On prolonged exposure to air the green crystals effloresce to a blue or bright-green hydrate with $6\text{H}_2\text{O}$ (also formed on heating with the saturated solution at 54°); above 280° yellow anhydrous NiSO_4 is formed. Like ferrous sulphate nickel sul-

phate readily forms double salts, the most important being the bluish-green **nickel ammonium sulphate** $(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ used in electroplating.

In the separation of cobalt and nickel in qualitative analysis use is made of the fact that cobalt forms a stable cobalticyanide $\text{K}_3\text{Co}(\text{CN})_6$ (p. 945), whilst nickel forms only the bright-red nickelocyanide $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$, not oxidised by boiling in air, easily decomposed by acids, and oxidised to black Ni_2O_3 by hypochlorite. Nitrite forms a soluble $\text{K}_4\text{Ni}(\text{NO}_2)_6$, but if calcium is present $\text{K}_2\text{CaNi}(\text{NO}_2)_6$ is precipitated and could be mistaken for potassium cobaltinitrite (p. 945). A very characteristic nickel compound is **nickel dimethylglyoxime** formed as a bright-red crystalline precipitate by adding a slight excess of α -dimethylglyoxime and then dilute ammonia to a solution of a nickel salt. It may be dried at 115° and weighed in the gravimetric determination of nickel. This compound contains 4-covalent nickel, the four valencies being in the same plane as the two rings :



α -diphenylglyoxime is an even more sensitive test (1 of Ni in 10^6) for nickel than dimethylglyoxime (0.01 mgm. Ni). A yellow precipitate is formed on addition of dicyandiamide $(\text{CN})_2(\text{NH}_2)_2$ and then potassium hydroxide to an acidified solution of a nickel salt.

The compounds $\text{BaM}^{\text{II}}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ ($\text{M}^{\text{II}} = \text{Ni}, \text{Pd}, \text{Pt}$) are isomorphous and the valencies in the ion $[\text{M}^{\text{II}}(\text{CN})_4]^{--}$ are *planar* (p. 422). This results from dsp^2 hybridisation of one d , one s and two p wave functions or orbitals (p. 436) :

	3d	4s	3p	
Ni	:	:	0 0 0	(Ni electrons = ·
Ni ⁺⁺	:	0	0 0 0	CN' electrons = ×
[Ni(CN) ₄] ⁻⁻	:	×	× × 0	vacant orbitals = 0)

A *tetrahedral* arrangement results from d^2s or sp^3 hybridisation, whilst d^2sp^3 gives six *octahedral* bonds (p. 423).

The **atomic weights of cobalt and nickel** are nearly the same but that of cobalt is slightly higher, whereas the atomic numbers are in the reverse order. The elements Fe, Co, Ni, however, have always been placed in this order in the Periodic Table because of the gradation of physical and chemical properties, and because of the resemblance between cobalt compounds and those of rhodium and iridium, elements occupying corresponding places in the other two transitional groups. The atomic weights of cobalt and nickel have been found by the reduction of the oxides, chlorides and bromides in hydrogen, and from the ratios $\text{CoCl}_2 : 2\text{AgCl}$ and $\text{NiBr}_2 : 2\text{AgBr}$. The valencies follow from the atomic heats and the vapour density of $\text{Ni}(\text{CO})_4$, as well as the isomorphism of cobalt and nickel compounds with those of other elements.

THE METAL CARBONYLS

The metal carbonyls proper are covalent compounds of metals with carbon monoxide. They form two main groups :

(A) Volatile, unimolecular, very soluble in non-polar solvents such as benzene.

Cr(CO) ₆	Fe(CO) ₅	Ni(CO) ₄
Mo(CO) ₆	yellow liquid,	colourless liquid,
W(CO) ₆	Ru(CO) ₅	
white crystals, rather stable and inert	colourless liquid	
	Os(CO) ₅	
	colourless liquid,	

(B) Non-volatile, all solid, polymerised, sparingly soluble in non-polar solvents.

[Re(CO) ₅] ₂	Fe ₂ (CO) ₉	[Fe(CO) ₄] ₂	[Fe(CO) ₃] _x
colourless	yellow, decomp. at 100°	dark-green, decomp. at 140°	red
	Ru ₂ (CO) ₉	[Co(CO) ₄] ₂	[Co(CO) ₃] ₄
	orange-yellow	orange, decomp. 52°	black, decomp. at 60°
	Os ₂ (CO) ₉	[Ru(CO) ₄] ₃	[Rh(CO) ₃] _x
	bright-yellow	green	red
		[Rh(CO) ₄] ₂	[Rh ₄ (CO) ₁₁] _x
		orange-yellow	black
		[Ir(CO) ₄] _x	[Ir(CO) ₃] _x
		greenish-yellow	yellow

General methods of preparation of metal carbonyls are :

(i) The action of carbon monoxide on the finely-divided metal at moderate temperature, in entire absence of oxygen. Except with nickel and iron the reaction is carried out under pressure.

(ii) The action of carbon monoxide under pressure on metal halides, in presence of copper or silver as halogen acceptor.

(iii) The reaction between the anhydrous metal chloride and phenyl magnesium bromide (C₆H₅MgBr (Grignard reagent) in dry ether, followed by passing in carbon monoxide gas and then hydrolysis. (This is the only method for chromium carbonyl.)

The most important carbonyls are nickel carbonyl Ni(CO)₄ (discovered by Mond, Langer and Quincke in 1888) and iron pentacarbonyl Fe(CO)₅ (discovered by Berthelot, and by Mond and Quincke, in 1891).

Nickel carbonyl Ni(CO)₄ is a colourless strongly refracting liquid, prepared by passing carbon monoxide over reduced nickel at 30°. It boils at 43.2° m. pt. - 25°, and gives the normal molecular weight either as vapour or in solution. The pure vapour explodes at 60°, carbon being deposited: Ni(CO)₄ = Ni + 2CO₂ + 2C. A mixture of the vapour and air is poisonous and explosive. Nickel carbonyl is best prepared under pressure, say 100 atm., which is favourable to the carbonyl side of the equilibrium: Ni + 4CO ⇌ Ni(CO)₄. At this pressure decomposition does not occur even at 250°. The equilibrium constant is [CO]⁴/[Ni(CO)₄] = K.

Nickel carbonyl is not decomposed by water free from air, or by dilute acids or alkalis. It is rapidly decomposed by halogens: Ni(CO)₄ + Br₂

NiBr₂ + 4CO; dry hydrogen chloride and bromide react very slowly but dry hydrogen iodide reacts as follows: Ni(CO)₄ + 2HI - NiI₂ + H₂ + 4CO.

Iron carbonyls.-When carbon monoxide is passed over finely-divided iron at 120°, iron pentacarbonyl Fe(CO)₅ is produced. It is a pale-yellow viscous liquid, b.pt. 102.5°, m.pt. -20°. The vapour is decomposed on passing through a tube heated to 180°, a mirror of metallic iron being deposited. The vapour density at 129° and the freezing point of the solution in benzene correspond with the above formula. Iron pentacarbonyl is decomposed by air and moisture and by acids: Fe(CO)₅ + H₂SO₄ = FeSO₄ + 5CO + H₂. On exposure to light, **diferro-nonacarbonyl** Fe₂(CO)₉ is formed, the reaction being reversed in darkness: 2Fe(CO)₅ = Fe₂(CO)₉ + CO. Fe₂(CO)₉ forms orange crystals, decomposing on heating: Fe₂(CO)₉ = Fe(CO)₅ + Fe + 4CO. If a solution of Fe₂(CO)₉ in toluene is heated to 50° it becomes intensely green and green crystals are deposited, which are a polymerised form of iron tetracarbonyl [Fe(CO)₄]₃. Iron pentacarbonyl is formed in traces when water-gas is passed through iron pipes or coal gas is stored under pressure in iron cylinders. Such gas deposits Fe₂O₃ on incandescent mantles in gas burners.

When iron pentacarbonyl is dissolved in barium hydroxide and the solution acidified, iron carbonyl hydride H₂Fe(CO)₄ is formed, which can be distilled in vacuum; it is acidic and a strong reducing agent:



A similar cobalt carbonyl hydride HCo(CO)₄ is formed from cobalt carbonyl [Co(CO)₄]₂ in the same way.

In the metal carbonyls the CO is linked covalently to the metal atom by the unshared pair of electrons on the carbon atom:



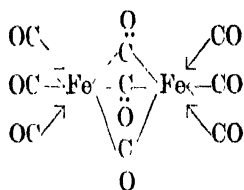
e.g. $\begin{matrix} \text{OC} \rightarrow \\ \text{OC} \end{matrix} \text{Ni} \begin{matrix} \leftarrow \text{CO} \\ \leftarrow \text{CO} \end{matrix}$ Langmuir (1921) pointed out an interesting relation between the *effective atomic number* (E.A.N.) - no. of electrons of metal + electrons donated by CO, and the electron shells of the inert gas at the end of the period in which the metal occurs:

	E.A.N.		
Ni(CO) ₄	28 + 8 =	36	Kr 36
Fe(CO) ₅	26 + 10 =	36	Kr 36
Ru(CO) ₆	44 + 10 =	54	Xe 54
W(CO) ₆	74 + 12 =	86	Rn 86

Since cobalt has 27 electrons it cannot form a carbonyl with an inert gas structure, but can form a **nitrosocarbonyl** Co(CO)₃(NO) by the donation of the odd electron of the NO to the metal to form 28 electrons, as in nickel, the residue of the NO and three CO molecules then forming coordinate links with four pairs of electrons. Co(CO)₃(NO) is thus analogous to Ni(CO)₄ and the two molecules have tetrahedral structures and very similar properties. Fe(CO)₅ has the structure of a trigonal bipyramid (p. 426).

The structures of the higher carbonyls are mostly unknown but Fe₂(CO)₉ is shown by X-ray analysis to have 6 CO molecules linked by coordination

and 3 CO groups joining the iron atoms by ordinary carbonyl linkages (Powell and Ewens, 1939) :



The carbonyl hydrides $\text{H}_2\text{Fe}(\text{CO})_4$ and $\text{HCo}(\text{CO})_4$ are tetrahedral and are supposed to be $\text{Fe}(\text{CO})_2(\text{COH})_2$ and $\text{Co}(\text{CO})_3(\text{COH})$, with the structure $\text{M}:\text{C}:::\text{O}:\text{H}$ for the COH linkage, the hydrogen being easily lost (Ewens and Lister, 1939).

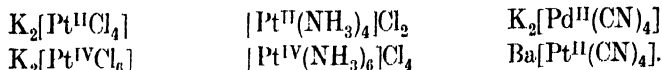
CHAPTER XLVIII

GROUP VIII METALS : THE PLATINUM METALS

THE two triads

44 Ru	45 Rh	46 Pd
76 Os	77 Ir	78 Pt

include metals all found in native platinum and hence called the *platinum metals*. Like other transitional elements they show varying valencies and ruthenium is notable in showing all valencies from 1 to the maximum 8. The valency 8 is shown by osmium in OsF_8 and OsO_4 and by ruthenium in RuO_4 , these compounds being all volatile. One or two valency states are usually most stable for each metal (see p. 913): the common palladium compounds are PdX_2 containing bivalent palladium; ruthenium and rhodium are most stable in the compounds RuX_3 and RhX_3 containing trivalent metals; platinum forms stable compounds PtX_2 and PtX_4 in which it is bivalent and quadrivalent. The platinum metals form many coordination and complex compounds:



Although the platinum metals are often regarded as "noble" metals like gold, this applies strictly only to platinum itself, since the other metals (especially if finely divided) all oxidise more or less when heated in air or oxygen, and ruthenium and osmium burn in oxygen on heating forming the volatile RuO_4 and OsO_4 , and iridium oxidises to a mixture of oxides.

PLATINUM

History.—Hieroglyphs on an Egyptian box discovered at Thebes, dating from the seventh century B.C., were found by Berthelot to be composed of an alloy of platinum, iridium and gold. Scaliger (1557) says there was found in Mexican mines a metal "which no fire or art of the Spaniards can bring to liquefaction," and this metal is again mentioned by Don Antonio de Ulloa, who visited Mexico in 1735. Specimens of platinum (called by the natives *platina de pinto*) were brought to Europe from Colombia in 1741 by Charles Wood and examined by William Brownrigg in 1750, by Lewis in 1754, by Marggraf in 1757, and by Bergman in 1777. Platinum foil and wire were first made in 1772 by Count von Sickingen, an ambassador in

Paris, and in 1806 they were sold in London for chemical purposes at 16s. an ounce.

Occurrence.—The deposits are in the Urals (discovered in 1823), California, Colombia, Borneo, and Australia (especially New South Wales). Platinum metals in the nickel ores of Sudbury, Ontario (p. 946), are extracted on an important scale as by-products in the Mond nickel process. Platinum occurs in several hard rocks in South Africa, but the native metal is usually obtained by washing alluvial sands and gravels. The concentrates are metallic grains or small nuggets, which in a Russian specimen had the following composition :

Platinum	Iridium	Rhodium	Palla- dium	Gold	Copper	Iron	Osm- mium	Sand
76.4	4.3	0.3	1.4	0.4	4.1	11.7	0.5	1.4

Osmiridium is a native alloy of osmium and iridium with small amounts of other metals :

Osmium	Iridium	Platinum	Rhodium	Ruthenium
27.2	55.2	10.1	1.5	5.9

It is insoluble in aqua regia and is very hard, so that it is used for the tips of the gold nibs of fountain-pens.

The gold is extracted from native platinum by amalgamation and the platinum metals digested with aqua regia. Osmiridium remains undissolved. The solution is evaporated to dryness and the residue heated at 125°. Palladium and rhodium then form the lower chlorides PdCl_2 and RhCl_3 . On treating with water, PdCl_2 , platinum chloride PtCl_4 and a little iridium chloride IrCl_4 , dissolve. The solution is acidified with hydrochloric acid and the chloroplatinic acid H_2PtCl_6 precipitated with ammonium chloride as the sparingly soluble ammonium salt $(\text{NH}_4)_2\text{PtCl}_6$. The other metals remain in solution. On heating ammonium chloroplatinate it decomposes, leaving spongy platinum. If this is heated to redness and hammered the sponge welds into a coherent mass. The metal may also be fused in the oxyhydrogen flame or in the electric furnace.

Properties.—Platinum is a tin-white metal of high density 21.4, and high melting point 1755°. It can be welded at a bright-red heat and may be rolled or drawn into wire. Very fine wires (Wollaston wires), down to 0.001 mm., are drawn inside a silver sheath, which can be dissolved off in nitric acid or by making the wire the anode in a solution of potassium argentocyanide. Platinum is resistant, but is attacked by carbon and phosphorus at a red heat, becoming brittle.

A smoky flame should not be used with platinum crucibles, nor magnesium pyrophosphate ignited along with the filter-paper, since in this case phosphorus is set free. Pure platinum is not attacked on heating in air, but some commercial metal loses weight appreciably and becomes grey and rough after heating. It is said to be appreciably volatile at 1300°, or even at 800° when exposed to air. Platinum which gains in weight on heating contains iron. Easily reducible metals such as tin and lead readily alloy with platinum, causing it to fuse, and compounds of these metals must not

be heated in platinum crucibles with filter-paper. Fused caustic alkalis, sulphides, and sodium peroxide also attack platinum, and it is slightly attacked by the fused carbonates, but not by hydrofluoric acid. Fused lithium and magnesium chlorides, potassium cyanide, and nitrates, attack platinum.

Pure platinum is not attacked by hot concentrated sulphuric acid, although the commercial metal is slightly soluble in it. It is dissolved by aqua regia on heating, especially if a large excess of concentrated hydrochloric acid is added. An alloy of platinum and lead dissolves completely in nitric acid. On evaporating the solution in aqua regia, moistening the residue with concentrated hydrochloric acid and re-evaporating, chloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$ is obtained in reddish-brown deliquescent crystals, commonly known as "platinum chloride." The product may contain $Pt(NO)_2Cl_4$.

Platinum has nearly the same coefficient of expansion as glass and may be sealed into it without causing cracking on cooling. The wires sealed into electric lamp bulbs were formerly platinum, but have been replaced by manganin, by copper coated with boron trioxide, or Eldred's wire, which has a core of nickel steel, a jacket of copper and an outer sheath of platinum or a fused film of potassium borate. Platinum is used in dentistry and in making jewellery, especially as a setting for diamonds. It is used for electrical contacts and as a catalyst in the manufacture of sulphur trioxide and the oxidation of ammonia. Tantalum has been proposed as a substitute for platinum in electrical contacts.

Platinum sponge is a grey porous form obtained by heating ammonium chloroplatinate. *Platinum black* is a finely-divided powder obtained by reducing a solution of chloroplatinic acid by zinc, or with sodium formate solution. These forms are very active catalytically. Alcohol is oxidised to aldehyde by platinum black, on account of its occluded oxygen, and a mixture of oxygen and hydrogen is exploded by platinum sponge or even by very clean foil.

Platinised asbestos is made by soaking asbestos fibres (previously boiled with concentrated hydrochloric acid) in platinum chloride solution, drying, and heating in a crucible with a little ammonium chloride, or reducing with sodium formate solution. *Colloidal platinum* is formed as a brown solution by causing small electric arcs to pass repeatedly between platinum wires under water, or by reducing a solution of platinum chloride with hydrazine in presence of sodium lysalbate, a protective colloid. The colloidal solution is a catalyst (see p. 195).

Compounds of platinum.—Platinum forms two series of compounds, the *platinous compounds* PtX_2 , and the more important *platinic compounds* PtX_4 .

Chloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$, the preparation of which is described above, is a strong dibasic acid: it gives with silver nitrate a yellow precipitate of silver chloroplatinate Ag_2PtCl_6 . The acid gives the ion $PtCl_6^{--}$, which on electrolysis migrates to the anode, although metallic platinum is deposited on the cathode as a result of the reducing action of the liberated hydrogen.

On heating potassium chloroplatinate chlorine is evolved and a residue of platinum and potassium chloride is left : $K_2PtCl_6 = 2KCl + Pt + 2Cl_2$. Ammonium chloroplatinate $(NH_4)_2PtCl_6$ leaves a residue of pure platinum on heating. Lithium and sodium chloroplatinates are soluble ; those of rubidium and caesium are less soluble than the potassium salt (p. 715).

Platinic chloride $PtCl_4$ is obtained as a reddish-brown crystalline mass when chloroplatinic acid is heated at 369° in chlorine or 165° in hydrogen chloride. At 390° in chlorine, greenish-black platinum trichloride $PtCl_3$ is obtained, and at 580° brownish-green platinum dichloride $PtCl_2$.

Platinum tetrachloride dissolves in water to a yellowish-red solution which seems to contain a complex acid $[PtCl_4(OH)_2]H_2$, since it forms a silver salt $[PtCl_4(OH)_2]Ag_2$. Crystals of $PtCl_4 \cdot 5H_2O$ may be obtained. Platinum dichloride is insoluble in water but dissolves in hydrochloric acid to a dark-brown chloroplatinous acid H_2PtCl_4 , also formed by the action of sulphur dioxide on chloroplatinic acid solution. It does not crystallise but forms an amorphous solid on evaporation.

Potassium chloroplatinite K_2PtCl_4 is obtained by warming a paste of potassium chloroplatinate K_2PtCl_6 with cuprous chloride. It forms dark-red crystals, used in photography. Paper is impregnated with a mixture of K_2PtCl_4 and ferric oxalate. On exposure to light the ferric oxalate is reduced to ferrous oxalate, and if the paper is developed in a solution of potassium oxalate a grey deposit of platinum is formed on the reduced parts ("platinotype").

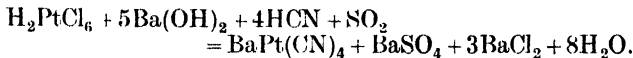
When sodium carbonate is added to chloroplatinic acid solution, and the residue after evaporation extracted with acetic acid, reddish-brown **platinic hydroxide**, really a complex compound $H_2[Pt(OH)_6]$, remains. This dissolves in hydrochloric acid to form $H_2[Pt(OH)_2Cl_4]$; silver acetate gives with the solution $Ag_2[Pt(OH)_6]$. Platinic hydroxide dissolves in potassium hydroxide to form **potassium platinate** $K_2[Pt(OH)_6]$, forming yellow crystals. On gently heating $H_2[Pt(OH)_6]$ black platinum dioxide PtO_2 is formed. **Platinum trioxide** is formed when a solution of potassium platinate, $K_2[Pt(OH)_6]$, in potassium hydroxide is electrolysed and the deposit on the anode, $K_2O \cdot 3PtO_3$, is extracted with cold acetic acid; PtO_3 is a brown powder which does not decompose H_2O_2 .

Alkalis precipitate from K_2PtCl_4 solution black **platinous hydroxide** $Pt(OH)_2$, probably complex, $H_2[Pt(OH)_4]$, soluble in hydrochloric acid. This has no acidic properties; on gentle heating it forms black **platinous oxide** PtO .

Potassium iodide does not give with chloroplatinic acid a precipitate of potassium chloroplatinate, but a dark-red clear solution. On heating, this deposits black **platinic iodide** PtI_4 , soluble in alcohol. When digested with hydriodic acid this forms **iodoplatinic acid** H_2PtI_6 , crystallising in black needles. Platinic iodide decomposes into iodine and platinum at 130° . **Platinous iodide** PtI_2 is obtained as a black powder by heating platinous chloride with potassium iodide solution.

Hydrogen sulphide gives with H_2PtCl_6 a black precipitate of **platinic sulphide** PtS_2 , soluble in yellow ammonium sulphide to a dark-brown solution of a **thioplátinate** $(NH_4)_4Pt^{IV}Pt^{IV}S_6$. Platinous salts give black **platinous sulphide** PtS .

Complex platinum compounds.—Numerous complex compounds of platinum are known. The **platinamines** contain molecules of ammonia combined with the metal atom as in the cobaltamines (p. 417); two series exist, corresponding with bivalent and quadrivalent platinum. **Barium platinocyanide** $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ is a lemon-yellow powder used for fluorescent screens in X-ray work. Baryta-water and hydrocyanic acid are added to chloroplatinic acid, the solution is warmed and treated with sulphur dioxide till colourless. BaSO_4 is filtered off and the filtrate crystallised :



Magnesium platinocyanide $\text{MgPt}(\text{CN})_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ is bright scarlet with green and purple reflected colours, but forms white $\text{MgPt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ at 100° .

Palladium.—When potassium or mercuric cyanide solution is added to the solution of native platinum in aqua regia a pale-yellow precipitate of **palladous cyanide** $\text{Pd}(\text{CN})_2$ is obtained, which on ignition leaves metallic palladium (Wollaston, 1803). The chief source of palladium is the Sudbury (Ontario) nickel ore. The metal is white and forms a white alloy with gold. Palladium oxidises superficially when heated in air, becoming covered with a blue film of **palladium monoxide** PdO , reduced again at a higher temperature. Palladium dissolves in dilute nitric acid forming **palladous nitrate** $\text{Pd}(\text{NO}_3)_2$, and in aqua regia forming **chloropalladic acid** H_2PdCl_6 , but on evaporation palladous chloride PdCl_2 is formed and no simple PdX_4 halides are known. Palladium dissolves in boiling concentrated sulphuric acid, forming **palladous sulphate** PdSO_4 . Potassium iodide precipitates black **palladous iodide** PdI_2 , soluble in excess to a brown solution. The tendency to the formation of palladous compounds is noteworthy and should be compared with the similar property of nickel. The absorption of hydrogen by palladium has been considered on p. 171.

Osmium and Iridium are contained in osmiridium (p. 954). If this is fused with sodium chloride in a current of chlorine, **osmic chloride** OsCl_4 volatilises. The solution of the residue in hydrochloric acid is treated with hydrogen; platinum and ruthenium are deposited. When more hydrogen is passed through the decanted green liquid, iridium is thrown down (Tenant, 1804).

Iridium is very hard and is used for the tips of gold pens. Iridium crucibles resist the action of carbon, phosphorus, and aqua regia. The standard metre of Paris was constructed by Johnson and Matthey, in London, from an alloy of 90 parts of platinum and 10 parts of iridium. The same alloy is used together with pure platinum in making thermocouples for the measurement of high temperatures. Since iridium volatilises above 1000° , an alloy of platinum and 10 per cent of rhodium is now used.

The Ir^{III} and Ir^{IV} compounds are stable, but there is a white **iridium pentafluoride** IrF_5 . **Iridium tetrachloride** IrCl_4 is reddish-black, giving a red solution from which potassium hydroxide precipitates dark-red K_2IrCl_6 . This dissolves in excess of alkali to an olive-green solution, which on warming becomes bright-green, rose-red, and violet, then depositing the intensely

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